STUDIES ON REACTIVITY AND LIGATING BEHAVIOR OF AROMATIC THIOAMIDES

A Thesis Submitted

In Partial Fulfilment of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

by

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to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

FEBRUARY, 1987

Dedicated

to

My Parents

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor S.K. Dikshit.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Veena Chauhan

Veena Chauhan

Kanpur
February 1987

CERTIFICATE

Certified that the work contained in this thesis entitled: "STUDIES ON REACTIVITY AND LIGATING BEHAVIOUR OF AROMATIC THIOAMIDES" has been carried out by Ms. Veena Chauhan, under my supervision and the same has not been submitted elsewhere for a degree.

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Thesis Supervisor

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CERTIFICATE OF COURSE WORK

This is to certify that Ms. Veena Chauhan has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

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Chm 524	Modern Physical Methods in Chemistry
Chm 525	Principles of Physical Chemistry
Chm 541	Advanced Inorganic Chemistry I
Chm 542	Advanced Inorganic Chemistry II
Chm 545	Principles of Inorganic Chemistry
Chm 800	General Seminar
Chm 801	Special Seminar
Chm 900	Post-Graduate Research

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VEENA CHAUHAN

PREFACE

In the past twenty years there has been a resurgence of interest in the general field of sulfur ligand chemistry. Stimulus for this work has undoubtedly arisen from various sources. Ligand systems having sulfur-donor atoms are chemically very versatile. With transition metal ions they form a wide variety of stable compounds that display interesting and often quite novel properties and structures. In addition, the biochemical importance of metal sulfur system has prompted much effort in areas such as model compound synthesis. The recent observation of involvement of sulfur containing molecules in conjunction with a few transition metal ions in various enzymatic and metabolic processes have given a further challenge to the chemists. Designing of the sulfur containing model molecules mimicing those involved in natural process ranks among the prime goals of inorganic chemistry.

The co-ordination chemistry of title ligands Aromatic Thioamides (ArCSNHCOR) is almost in its infancy and only within the past few years has some understanding of the properties of these ligands been gained. The impetus for this work arises from the wide ranging application of sulfur and nitrogen containing ligands in medicine and the possibility of their metal complexes having anti-tumor and anti-cancer activity. In addition such molecules invariably possess diverse co-ordinating potential.

The title ligands are capable of existing in three tautomeric forms and clearly possess a variety of co-ordinating possibilities. The eventual outcome of a particular interaction of ambidentate ligand with metal ions is a function of the character of the cation and the reaction condition. This class of ligands are very versatile and exhibit a great variety of co-ordination modes. The present thesis is an attempt to explore the reactivity and the structural aspect of their metal complexes. This is proposed to get drug-test done on the complexes and study the interconversion between complexes having different modes of bonding of the title ligands.

The thesis begins with a chapter on a brief literature survey related to the present understanding of thioamide bands and their application in deciding bonding site.

In the second chapter, the synthetic details and characterization of N-carboethoxy-4-toluenethioamide (Hctt) complexes of various transition metal ions of first, second and third transition series are given. Abstraction of sulfur from the ligand by soft metal ions, e.g., Ag(I), Cu(II), Cd(II), Hg(II) is also described.

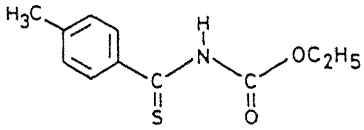
The third chapter encompasses the reactions of transition metal ions with N-carboethoxy-1-pyrrolethioamide (Hcpt) under different conditions.

Chapter four describes the substitution reactions of $[CuX(MPh_3)]$ with several aromatic thioamides and 2-thiopyrrole-1,2-dicarboximide.

Chapter five describes the substitution reactions of $[RuCl_2(PPh_3)_3]$ and $[(\eta^5-C_5H_5)RuCl(AsPh_3)_2]$ with several aromatic thioamides and 2-thione-3-phenyl-4-quinazolinone, 2-thiopyrrole-1,2-dicarboximide and addition reactions of $[RuCl_2(CO)_2]$ with the above ligands.

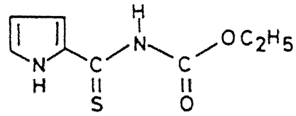
ABBREVIATIONS

(i)



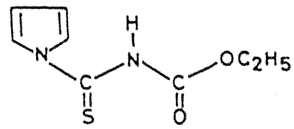
N-carboethoxy-4-toluene thioamide (Hctt)

(ii)



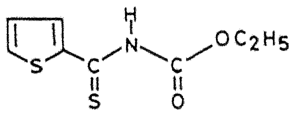
N-carboethoxy-2-pyrrole thioamide (Hcept)

(iii)



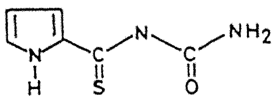
N-carboethoxy-1-pyrrole thioamide (Hcpt)

(iv)



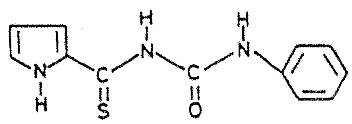
N-carboethoxy-2-thiophene thioamide (Hcett)

(v)



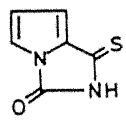
N-carboamido-2-pyrrole thioamide (Hcapt)

(vi)

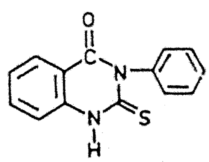


N-carbophenylamido-2-pyrrole thioamide (Hcppt)

(vii)



2-Thiopyrrole-1, 2-dicarboximide (Htp)



(viii) 2-thione-3 phenyl-4-quinazolinone (Htpq)

SYNOPSIS

Recently a considerable research effort has been directed towards the synthesis and structural characterization of metal complexes of aromatic thioamide ligands (ArCSNHCOR).[1-6] These studies have been stimulated by a desire to understand more clearly the electronic & steric factors which influence the stoichiometries, geometries and reactivities of metal complexes having sulfur as one of the donor sites. The long term aim of this type of research is an understanding of the chemistry of this important class of ligands. More specifically, it will be worthwhile to explore the relative importance of various resonance and tautomeric forms of the ligands for different metal ions and their contribution to the electronic structure of the resulting coordination compounds. In addition, it will be interesting to study the changes in both chemical reactivity and structural properties of aromatic thioamides and their complexes induced by alteration in the peripheral structure of the coordinated ligand.

The first chapter gives survey of the literature on the current understanding of thioamide absorption bands and their contribution to illumination of bonding sites. In addition the present status of coordination chemistry of the title and similar ligands, is also provided.

In the second chapter, the reactions of N-carboethoxy-4-toluenethioamide (Hctt) with several transition and non-

transition metal ions are described. The ligand reacts with bivalent (Ni, Co, Cu, Ru, Pd and Pt) and trivalent (Ru and Rh) metal ions, giving $M^{II}(ctt)_2$, $Ru^{III}(ctt)_3$ and $Rh^{III}Cl_2(ctt)$-(Hctt). In the presence of pyridine, the reactions of Co(II) and Ni(II) salts with Hctt lead to the formation of $M^{II}(ctt)_2py$. $[Rh^{I}Cl(PPh_3)_3]$, $[Pd(PPh_3)_4]$ and $[Pt(PPh_3)_4]$ react with Hctt to yield $[RhCl(Hctt)_2(PPh_3)]$, $[Pd(Hctt)_2(PPh_3)_2]$ and $[Pt(Hctt)_2$-$(PPh_3)_2]$ respectively. The soft metal ions such as Ag(I), Cu(II), Pd(II), Hg(II) and Cd(II) under reflux conditions abstract sulfur from Hctt and yield corresponding sulfide along with oxygenated form of the ligand (N-carboethoxy-4-toluene-amide). The i.r. spectra of the complexes indicate that the Hctt behaves as monoionic bidentate ligand, except in the cases of Rh(I), Rh(III), Pd(0) and Pt(0). In the complexes of Rh(I), Pd(0) and Pt(0), the Hctt is coordinated as neutral ligand through its S atom, whereas in Rh(III) complex through N and S atoms. All the complexes discussed in this chapter possess normal magnetic properties. The diamagnetism of $Ni(ctt)_2$ indicates its square planar geometry.

The third chapter deals with the reactions of N-carbo-ethoxy-1-pyrrole-thioamide (Hcpt) with several transition and non-transition metal ions. Complexes of the formulae $[M^{II}(cpt)_2]$ (M = Cu, Ni, Pd and Pt); $[M^{II}(cpt)_2py]$ (M = Ni and Co); $[M^{III}Cl(cpt)_2(H_2O)]$ (M = Ru and Rh); $[Ag^{I}(cpt)]$ and $[Rh^{I}Cl$-$(Hcpt)(PPh_3)]_2$ have been synthesized and characterized. Behaviour of Hcpt towards soft metal ions is similar to that of Hctt.

In Chapter four, the substitution reactions of $[Cu(MPh_3)_3X]$ (M = P or As; X = Cl^-, Br^- or I^-) with several thioamides ($R_1CSNHCOR_2$; R_1 = 1-pyrrole, 2-pyrroles, 4-tolyl; R_2 = OC_2H_5), N-carboamido-2-pyrrolethioamide and 2-thiopyrrole-1,2-dicarboximide are described. In these reactions, one triphenylphosphine/arsine molecule of $[Cu(MPh_3)_3X]$ is replaced by one ligand molecule. All the complexes described in this chapter are tetrahedral and invariably coordinated through S atom of the ligand molecule. They are diamagnetic in nature and soluble in most of the organic solvents. In all twenty eight complexes of Cu(I) are reported.

In the last chapter, the reactions of $[RuCl_2(CO)_2]$, $[(\eta^5\text{-}C_5H_5)RuCl(AsPh_3)_2]$ and $[RuCl_2(PPh_3)_3]$ with seven aromatic thioamide ligands and 2-thione-3-phenyl-4-quinazolinone are investigated. $RuCl_2(PPh_3)_3$ gives $RuCl_2(\text{ligand})(PPh_3).xCH_2Cl_2$ (x = 0, 1/2 or 1). Oxidation state of ruthenium was established with the help of magnetic susceptibility and esr studies. These reactions were carried out in dry N_2 atmosphere. Similarly the reactions of the ligands with $[(\eta^5\text{-}C_5H_5)RuCl(AsPh_3)_2]$ and $[RuCl_2(CO)_2]$ led to the formation of the diamagnetic compounds of the type $[(\eta^5\text{-}C_5H_5)RuCl(AsPh_3)(\text{ligand}).xCH_2Cl_2]$ (x = 0 or 1/2) and $[RuCl_2(CO)_2(\text{ligand})]$ respectively. The presence of dichloromethane in the compounds was confirmed with the help of ^1H NMR spectral studies apart from chemical analyses. The coordination mode(s) of the ligands were established on the basis of IR and ^1H NM

spectral data. All the Ru(II) diamagnetic complexes have been assigned distorted octahedral geometry.

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CONTENTS

CHAPTER I

INTRODUCTION

Aromatic thioamide ligands containing secondary thiamide (HN-C=S) groups are known to form complexes with transition and non-transition metals in various oxidation states.[1-5] Since the last decade our group has been actively engaged in exploring the ligating behaviour of aromatic thioamides and the reactivity of the complexes so formed. It has long been known that number of important biological processes involve metal ions which coordinate with a wide variety of ligands having sulfur, nitrogen and oxygen atoms as donor sites. Particularly HN-C=S groups not only play significant role in them but have very important pharmacological properties[6-9] as well. These ligands are usually polyfunctional in nature and are capable of trapping metal ions in an organic sphere. They have been found to show antiviral, anticancer and antitumour activities[10,11] in the biological systems. In order to understand these biological processes, there has been an increasing interest in the design and syntheses of new model complexes of properties similar to ones found in the biological processes. A large amount of work has been carried out to

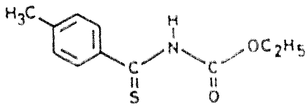
understand the coordinating nature of thioamide group, i.e., the donor properties of sulfur or nitrogen or simultaneous involvement of both sulfur and nitrogen. The nature of metal-sulfur bond and the position of ligands in spectrochemical and nephelauxetic series, etc. have not yet been well understood. Mono-thio and dithio-β-diketones have been used as ligands with nearly all the metals and possess very interesting properties. But very little work[12-14] has been done on the study of the effects on these properties if one changes CH group of $R_1CXCH_2CX'R_2$ (R_1,R_2 = substituents of wide variety; X,X' = S, O) by a more electronegative atom like nitrogen. As a result of this substitution new class of aromatic thioamide ligands ArCSNHCOR are obtained.

The present work is an attempt to explore, at least partially, the following aspects of ArCSNHCOR type of ligands: (i) A great variety of coordination modes of these versatile ligands as neutral molecule or monoanion and the possibility of the interconversion among different modes of bonding; (ii) the nature of the metal-sulfur, metal-nitrogen and metal-oxygen linkage; (iii) the position of the metals and the ligands in the nephelauxetic and spectrochemical series; (iv) stereochemistry and coordination number of the transition metal ions; (v) the stability of the square planar complexes with the ligands having delocalized π-electron systems; (vi) the relative importance of various resonance and tautomeric forms of the ligand for different metal ions and their contribution to the electronic structure of the

resulting coordination compound, and (vii) changes in both chemical reactivity and structural properties of aromatic thioamide ligands and their complexes induced by alteration in the peripheral structure of the coordinated ligands.

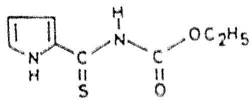
Complexing behavior of the following ligands has been investigated:

(i)



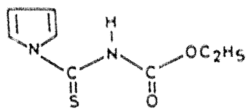
N-carboethoxy-4-toluene thioamide (Hctt)

(ii)



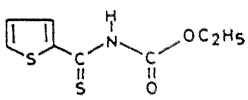
N-carboethoxy-2-pyrrole thioamide (Hcept)

(iii)



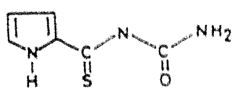
N-carboethoxy-1-pyrrole thioamide (Hcpt)

(iv)



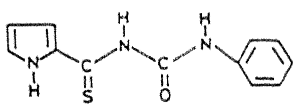
N-carboethoxy-2-thiophene thioamide (Hcett)

(v)



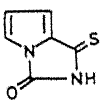
N-carboamido-2-pyrrole thioamide (Hcapt)

(vi)

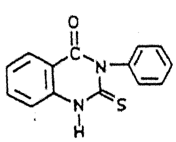


N-carbophenylamido-2-pyrrole thioamide (Hcppt)

(vii)



2-Thiopyrrole-1,2-dicarboximide (Htp)



(viii) 2-thone-3 phenyl-4-quinazolinone (Htpq)

These ligands have been prepared by the reaction of isothiocyanate esters with different heterocycles. Isocyanates and isothiocyanate esters are well established synthetic reagents and occupy a distinct position in the synthetic chemistry of hereocycles. Amongst these, alkoxycarbonyl isothiocyanates occupy a place of particular interest. The strong electron withdrawing power of the ethoxycarbonyl group increases the reactivity of the adjacent isothiocyanate function so that the usual nucleophilic addition at this moiety will be promoted. Moreover, the bifunctional nature of these systems enables them to participate in a variety of condensation-cyclization reactions peculiar to themselves. As a consequence they have become tremendously useful in heterocyclic syntheses. Ethoxycarbonyl isothiocyanate commonly known as ECIT, reacts with most of the nucleophilic compounds at the isothiocyanate group to form products incorporating the thioamide group. In the presence of $AlCl_3$, ECIT reacts with aromatic compounds to form N-ethoxycarbonyl thioamides:[15]

$$\mathrm{RH} \;+\; \mathrm{SCNCOOEt} \xrightarrow[\substack{CH_2Cl_2,\\ 0-3^{\circ}}]{AlCl_3} \mathrm{R{-}\underset{\underset{S}{\|}}{C}{-}NHCOOEt}$$

R = Ph, 4-MeC_6H_4, 4-EtC_6H_4, 4-i-PrC_6H_4, 4-t-BuC_6H_4, 2-5 $Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4

N-Carboethoxy-2-pyrrole thioamide (1)[16] is obtained in high yield when pyrrole is allowed to react with ethoxycarbonyl isothiocyanate. Oxidation of 1 with alkaline hydrogen peroxide

yields the expected N-carboethoxy-2-pyrroleamide (2), but treatment with hydrogen peroxide in acetic acid leads to N-carboethoxy-2-pyrrolethioamide S-oxide (3).

Compound 1 shows considerable reactivity towards nucleophilic reagents at both the carbonyl and thiocarbonyl groups. Thus heating with aqueous sodium hydroxide hydrolyses the ester group with loss of CO_2 and formation of pyrrole-2-thiocarboxamide (4) in excellent yield. Boiling with aniline for a few minutes results in the substitution at the carbonyl and yields N-carbophenylamido-2-pyrrolethioamide (6). The compound 6 is readily oxidized to the known N-carbophenylamido-2-pyrroleamide (7) by hydrogen peroxide.

When 1 is heated with quinoline it undergoes cyclization resulting in the elimination of EtOH and the formation of 2-thiopyrrole-1,2-dicarboximide (14). By the action of hydrogen peroxide in acetic acid, 14 is converted to 2-thiopyrrole-1,2-dicarboximide S-oxide (15) and when alkaline H_2O_2 is used, 14 is oxidized to pyrrole-1,2-dicarboximide (13). Prolonged treatment with P_4S_{10} in refluxing xylene converts both 13 and 14 into pyrrole-1,2-dithiocarboximide (16).

Nucleophilic reagents attack 14 at either the carbonyl or the thiocarbonyl group. In the first instance, the thiohydantoin ring opens between carbonyl and pyrrole nitrogen, yielding derivatives of pyrrole-2-thiocarboxamide, in complete

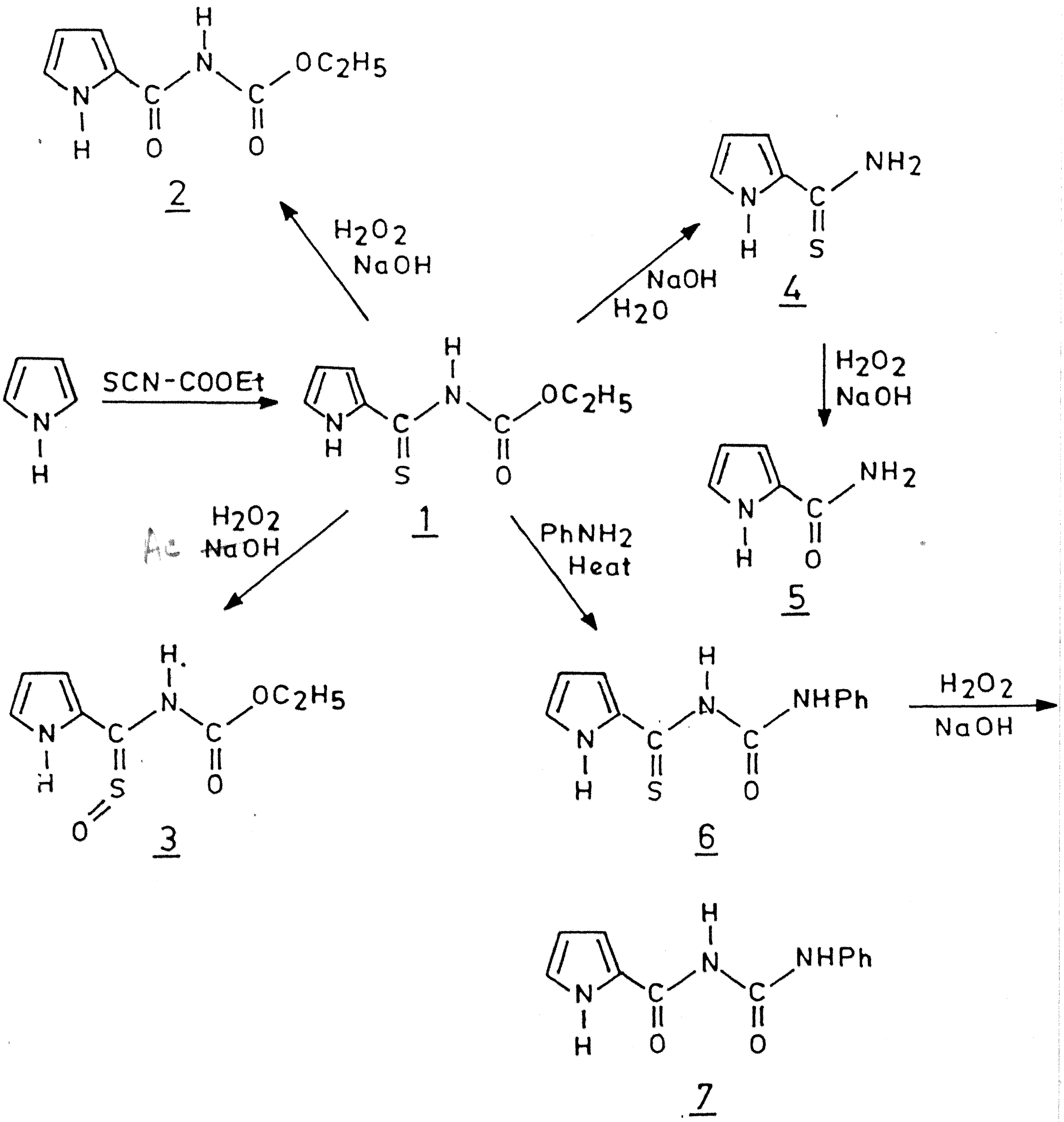
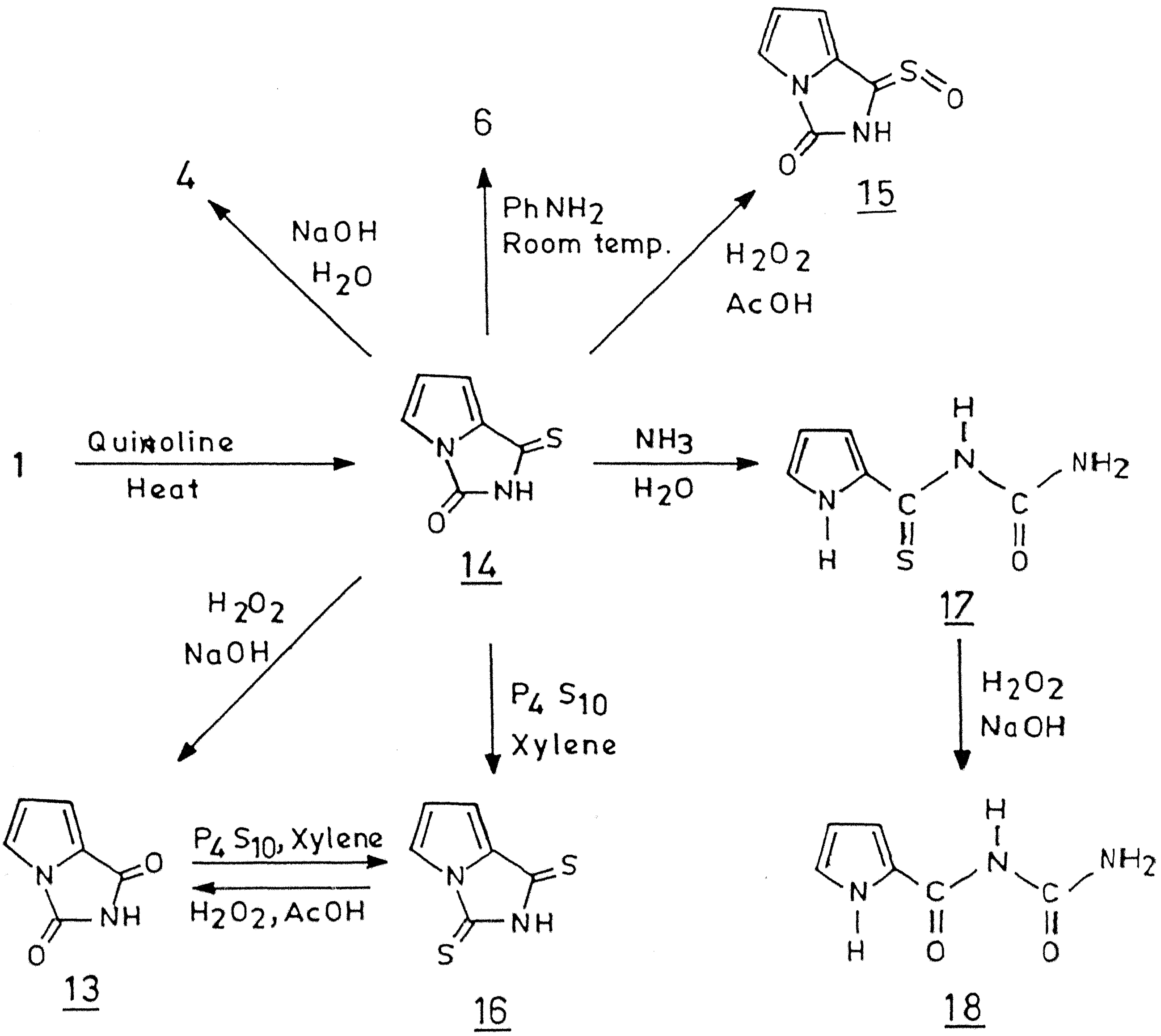


Fig. I.1

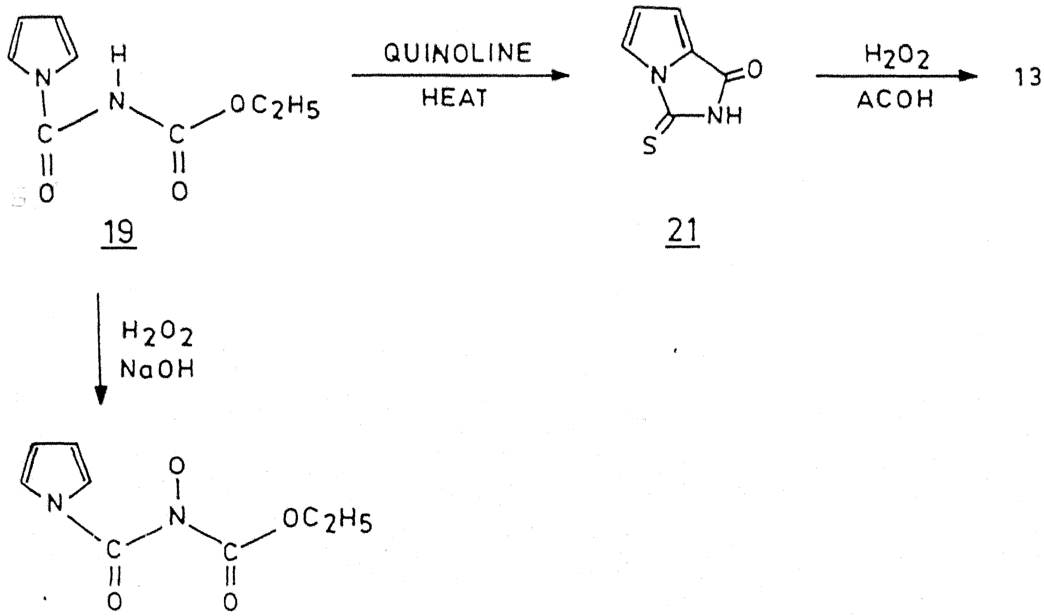


15
6
4
NaOH
H_2O
$PhNH_2$
Room temp.
H_2O_2
AcOH
1
Quinoline
Heat
14
NH_3
H_2O
17
H_2O_2
NaOH
P_4S_{10}
Xylene
H_2O_2
NaOH
P_4S_{10}, Xylene
H_2O_2, AcOH
13
16
18

Fig. I.2

analogy with the behaviour of pyrrole-1,2-dicarboximide (13). Thus, treatment with aqueous NH_3 converts 14 to N-carboamido-2-pyrrolethioamide (17). Oxidation of 14 to the known N-carbo-amido-2-pyrroleamide (18) is achieved with hydrogen peroxide (vide supra, Figs. I.1 and I.2).

Treatment of potassium salt of pyrrole with ethoxycarbonyl isothiocyanate leads to the reaction at the ring nitrogen and the formation of N-carboethoxy-1-pyrrolethioamide (19). In many respects, the reactivity of this compound parallels that ot its isomer 1 . Thus, it is oxidized readily to N-carboethoxy-1-pyrroleamide (20) by hydrogen peroxide. Boiling 19 with quinoline for a few minutes causes ring closure at position 2 of the pyrrole ring and yields 1-thiopyrrole-1,2-dicarboximide (21). Oxidation of this compound with hydrogen peroxide in acetic acid gives pyrrole-1,2-dicarboxamide (13).



Thiophene, a structural analogue of pyrrole reacts with isocyanates at position 2, but its reactivity towards ethoxycarbonyl isothiocyanates has been found to be much less pronounced. The reaction undergoes only in the presence of anhydrous stannic chloride[17] to yield the condensed product. The reactivity of thiophene towards ethoxycarbonyl isothiocyanate has been found to be less pronounced than that of pyrrole. However, on momentarily boiling with aniline the reaction occurs at ester carbonyl to give N-carbophenylamido-2-thiophenethioamide. As in the case of corresponding pyrrole derivatives the thiocarbonyl group shows considerable reactivity towards ammonia, primary and secondary amines.

The metal ions choosen here for the study of ligating behaviour are: Co(II), Co(III), Ni(II), Cu(I), Cu(II), Ru(II), Ru(III), Rh(I), Rh(III), Pd(0), Pd(II), Pt(0), Pt(II), Pt(IV), Ag(I), Pb(II), Cd(II) and Hg(II).

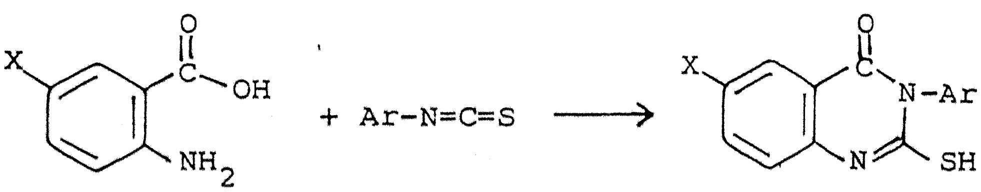
Both monoanions and neutral molecules of these ligands act as mono, bi or tridentate depending upon the metal ions and the reaction conditions. The simultaneous participation of all the donor atoms in the bond formation is virtually impossible because of electronic and stereochemical factors. This could be possible when the ligands are bonded to two metal ions simultaneously. The complexes synthesized have been characterized by elemental analyses, conductance, magnetic susceptibility studies and variety of spectroscopic techniques (infrared, electronic, proton n.m.r.,

^{31}P n.m.r). Their possible structures have been tentatively proposed and given in Table I.1.

2-Thione-3-phenyl-4-quinazolinone

The quinazolinone and quinazoline derivatives have been studied extensively by several workers.[18] Some of them were found to be biologically active and have been used as antimalarials. These were screened against blood induced *P. gallinacenum* in 7 days old chicks. The substituted quinazolinones have also been used as hypnotic agents in rats.[19,20]

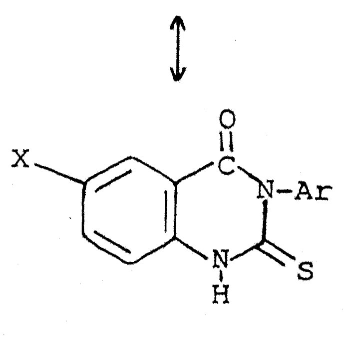
Generally, 6-(substituted/unsubstituted)-2-thio-3-aryl-4-quinazolinones, are prepared[21] by condensation of 5-(substituted/unsubstituted)anthranilic acid with monosubstituted(-aryl-substituted) phenylurea (heating 2 hrs at 180-190°C) or with aryl-isothiocyanate (refluxing 1-2 hrs in EtOH) in 50-70% yield.



I

X = H, Cl, I

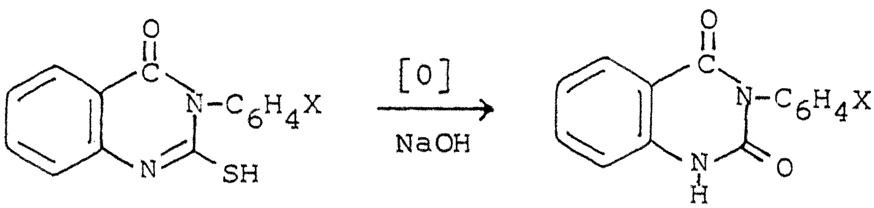
Ar = H, Ph, 3-MeC_6H_4, 4-MeC_6H_4, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, -$HOOCC_6H_4$



II

The 5-substituted-2-mercapto-3-aryl-4-quinazolinones were synthesized from anthranilic acid, aryl-isothiocyanates and alkyl halides.[19]

The action of some oxidizing agents such as $KMnO_4$, H_2O_2 and chlorine on 2-mercapto-3-aryl-4-quinazolinones in alkaline medium gave the corresponding keto compounds.[22]



III

The metal ligand bond will have partial ionic and partial covalent character which will vary within limits from bond to bond. The possibility of metal ligand bond to be purely ionic or covalent is ruled out for the following reasons: (i) the metal and ligand coordinating atoms are of different sizes, (ii) they have different electronegativities, (iii) they have different polarizabilities. Besides σ type of covalent bonds, there is possibility of π-bond formation ($d\pi-p\pi$ or $d\pi-d\pi$) in metal complexes (either $M \rightarrow L$ or $L \rightarrow M$). Since the overlap is considerably more effective along the internuclear axis than off it, π-bonds will be weaker than σ bonds and they do not generally exist independently. However, the formation of π-bonds will tend to draw the nuclei involved closer together with a consequent increase in the σ overlap and hence an overall gain in bond energy, resulting in the

Table I.1. Formula, structure, bonding scheme and colour of the complexes

Sl. No.	Compound	Structure	Bonding	Colour
1.	$[Ni(ctt)_2]$	Square planar	B	Brown
2.	$[Ni(ctt)_2py]$	Square pyramidal	B	Dark brown
3.	$[Co(ctt)_2]$	Square planar	C	Black brown
4.	$[Co(ctt)_2py]$	Square pyramidal	C	Dark greenish
5.	$[Cu(ctt)_2]$	Square planar	C	Brown
6.	$[Ru(ctt)_3]$	Octahedral	B	Black
7.	$[Ru(ctt)_2]$	"	B	Reddish brown
8.	$[Rh(ctt)(Hctt)Cl_2]$	"	C	"
9.	$[RhCl(Hctt)_2(PPh_3)]$	Square planar	D	Yellow
10.	$[Pd(ctt)_2]$	"	B	Yellowish brown
11.	$[Pd(Hctt)_2(PPh_3)_2]$	Tetrahedral	A	Yellow
12.	$[Pt(ctt)_2Cl_2]$	Octahedral	C	Brown
13.	$[Pt(ctt)_2]$	Square planar	C	Yellow
14.	$[Pt(Hctt)_2(PPh_3)_2]$	Tetrahedral	A	Orange
15.	$[Cu(cpt)_2]$	Square planar	B	Light bro
16.	$[Ni(cpt)_2]$	"	B	Yellow
17.	$[Ni(cpt)_2\ y]$	Square pyramidal	B	Green
18.	$[Co(cpt)_2\ y]$	"	B	Brown
19.	$[Ag(cpt)]$	Linear (polymeric)	C	Yellow
20.	$[RuCl(cpt)_2(H_2O)]$	Octahedral	C	Black brown

...contd.

Table I.1 (contd.)

Sl. No.	Compound	Structure	Bonding	Colour
21.	$[RhCl(cpt)_2(H_2O)]$	Octahedral	C	Reddish brown
22.	$[RhCl(Hcpt)(PPh_3)]_2$	Square planar (dimeric)	D	Yellow
23.	$[Pd(cpt)_2]$	Square planar	C	Yellow
24.	$[Pt(cpt)_2]$	"	C	Dark brown
25.	$[CuCl(Hctt)(PPh_3)_2]$	Tetrahedral	A	Red
26.	$[CuBr(Hctt)(PPh_3)_2]$	"	A	Red
27.	$[CuI(Hctt)(PPh_3)_2]$	"	A	Red
28.	$[CuCl(Hctt)(AsPh_3)_2]$	"	A	Dark orange
29.	$[CuBr(Hctt)(AsPh_3)_2]$	"	A	Orange
30.	$[CuI(Hctt)(AsPh_3)_2]$	"	A	Orange
31.	$[CuCl(Hcept)(PPh_3)_2]$	"	A	Orange
32.	$[CuBr(Hcept)(PPh_3)_2]$	"	A	Orange
33.	$[CuI(Hcept)(PPh_3)_2]$	"	A	Orange
34.	$[CuCl(Hcept)(AsPh_3)_2]$	"	A	Maroon
35.	$[CuBr(Hcept)(AsPh_3)_2]$	"	A	Maroon
36.	$[CuI(Hcept)(AsPh_3)_2]$	"	A	Maroon
37.	$[CuCl(Hcpt)(PPh_3)_2]$	"	A	Yellow
38.	$[CuBr(Hcpt)(PPh_3)_2]$	"	A	Yellow
39.	$[CuCl(Hcpt)(AsPh_3)_2]$	"	A	Yellow
40.	$[CuBr(Hcpt)(AsPh_3)_2]$	"	A	Yellow
41.	$[CuCl(Htp)(PPh_3)_2]$	"	A	Dark red
42.	$[CuBr(Htp)(PPh_3)_2]$	"	A	Dark red

...contd.

Table I.1 (contd.)

Sl. No.	Compound	Structure	Bonding	Colour
43.	$[CuI(Htp)(PPh_3)_2]$	Tetrahedral	A	Dark red
44.	$[CuCl(Htp)(AsPh_3)_2]$	Tetrahedral	A	Brown
45.	$[CuBr(Htp)(AsPh_3)_2]$	"	A	Reddish brown
46.	$[CuI(Htp)(AsPh_3)_2]$	"	A	"
47.	$[CuCl(Hcapt)(PPh_3)_2]$	"	A	Yellow
48.	$[CuBr(Hcapt)(PPh_3)_2]$	"	A	Yellow
49.	$[CuI(Hcapt)(PPh_3)_2]$	"	A	Yellow
50.	$[CuCl(Hcapt)(AsPh_3)_2]$	"	A	Brown
51.	$[CuBr(Hcapt)(AsPh_3)_2]$	"	A	Brown
52.	$[CuI(Hcapt)(AsPh_3)_2]$	"	A	Brown
53.	$[RuCl_2(CO)_2(Hctt)]$	Octahedral	C	Yellowish brown
54.	$[RuCl_2(CO)_2(Hcept)]$	"	E	Brown
55.	$[RuCl_2(CO)_2(Hcpt)]$	"	C	Brown
56.	$[RuCl_2(CO)_2(Hcett)]$	"	C	Reddish brown
57.	$[RuCl_2(CO)_2(Hcapt)]$	"	B	Brown
58.	$[RuCl_2(CO)_2(Hcppt)]$	"	B	Yellowish brown
59.	$[RuCl_2(CO)_2(Htp)]$	"	C	Reddish brown
60.	$[RuCl_2(CO)_2(Htpq)]$	"	C	Light yellow
61.	$[RuCl_2(Hctt)(PPh_3)]\cdot\frac{1}{2}CH_2Cl_2$	Quasi-octahedral	D	Maroon
62.	$[RuCl_2(Hcept)(PPh_3)]$	Quasi-octahedral	D	Maroon
63.	$[RuCl_2(Hcpt)(PPh_3)]$	"	D	Dirty yellow

...contd.

Table I.1 (contd.)

Sl. No.	Compound	Structure	Bonding	Colour
64.	$[RuCl_2(Hcett)(PPh_3)]$	Quasi-octahedral	D	Violet
65.	$[RuCl_2(Hcapt)(PPh_3)]$	"	D	Brick red
66.	$[RuCl_2(Hcppt)(PPh_3)]$-1/2 CH_2Cl_2	"	D	Maroon
67.	$[RuCl_2(Htp)(PPh_3)]$-CH_2Cl_2	"	D	Bluish violet
68.	$[RuCl_2(Htpq)(PPh_3)]$	"	D	Yellow
69.	$[(\eta^5$-$C_5H_5)RuCl(Hctt)$-$(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	Distorted octahedral	D	Yellow brown
70.	$[(\eta^5$-$C_5H_5)RuCl(Hcept)$-$(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	"	D	Maroon
71.	$[(\eta^5$-$C_5H_5)RuCl(Hcept)$-$(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	"	F	Grey
72.	$[(\eta^5$-$C_5H_5)RuCl(Hcett)$-$(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	"	F	Violet
73.	$[(\eta^5$-$C_5H_5)RuCl(Hcapt)$-$(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	"	D	Reddish violet
74.	$[(\eta^5$-$C_5H_5)RuCl(Hcapt)$-$(AsPh_3)]$	"	D	Orange
75.	$[(\eta^5$-$C_5H_5)RuCl(Hcppt)$-$(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	"	D	Dark violet
76.	$[(\eta^5$-$C_5H_5)RuCl(Hcppt)$-$(AsPh_3)]$	"	D	Orange

....contd.

Table I.1 (contd.)

Sl. No.	Compound	Structure	Bonding	Colour
77.	$[(\eta^5-C_5H_5)RuCl(Htp)-(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	Distorted octahedral	D	Violet
78.	$[(\eta^5-C_5H_5)RuCl(Htpq)-(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	"	F	Yellow

A, Ligand is acting as unidentate and bonded through sulfur of the thioamide group.

B, Ligand is acting as bidentate, chelating ligand, bonded through oxygen and nitrogen atoms of the thioamide group to one metal atom.

C, Ligand is acting as bidentate, chelating ligand bonded through sulfur and nitrogen atoms of the thioamide group to one metal atom.

D, Ligand is acting as unidentate and bonded through oxygen of the thioamide group.

E, Ligand is acting as bidentate, chelating ligand bonded through sulfur and oxygen.

F, Ligand is acting as unidentate and bonded through nitrogen of the thioamide group.

shortening of σ bond. Further, the formation of π-bond will also contribute towards reduction in the mutual repulsions of the non-bonding electrons and thus strengthening the bond between metal and ligand. There is a controversy regarding back-bond formation. Thus, in the complexes of phosphine or arsine, for example, the situation is not clear and general opinion is against extensive π backbonding.

The strength and stability of a bond between the metal ion and the donor atom would depend upon several factors like size, electronegativity, the nature of orbitals involved and their overlapping capacity etc. The number and the nature of the substituents attached to the ligand donor atoms will also influence the stability of the bond between metal ions and the donor atoms. Much useful information regarding the metal-ligand interactions can be obtained from an evaluation of Dq and $\beta\,(\frac{B'}{B})$ using electronic spectra of metal complexes. The value of nephelauxetic ratio β, found from the electronic spectrum gives the extent of covalence in the metal-ligand bonds and helps in assigning the position of the ligand in the nephelauxetic series. The effect of covalence is to delocalize the metal ion electron density onto the ligand and thus reduce electron-electron repulsions of the d electrons in the complexed metal ion compared to the repulsion in the gaseous state ($B'/B < 1$) and the ratio decreases with increasing delocalization or cloud expanding. The crystal field splitting, obtained from the analysis of the spectra, decides the

position of the ligand in Fajans-Tsuchida spectrochemical series. The success of the method depends on the appearance of the expected bands based on Orgel or Tanabe-Sugaro diagrams. In some cases, these d-d transitions are obscured by strong charge transfer or intraligand bands. Thus, calculation of these very informative and useful spectral parameters may not be possible.

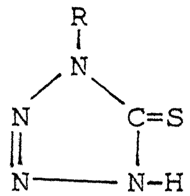
The i.r. spectral data have been extensively used for determining the bonding modes in metal complexes with variety of ligands. This class of ligands show systematic shifts in ν_{NH}, $\nu_{C=O}$, $\nu_{C=S}$ and four thioamide bands after complexation. Four thioamide bands I ($\nu_{C\cdots N}$ + δ_{NH}); II ($\nu_{C\cdots N}$ + δ_{C-H} + δ_{NH}); III ($\nu_{C\cdots N}$ + $\nu_{C\cdots S}$) and IV ($\nu_{C=S}$) have been found to be immensely useful in identifying the donor sites. The contributing vibrational modes of these four thioamide bands differ slightly in various reports in the literature. These bands lie approximately in the region 1500-750 cm^{-1}.

It will be worthwhile to review briefly the utility of thioamide bands and other relevant bands in ascertaining the donor sites in ligands having secondary thioamide group. Some illustrative examples are described in the following paragraphs.

<u>1-Substituted tetrazoline-5-thiones</u>[23,24]*

ML_2 type of complexes are obtained with Ni(II), Co(II), Cu(II) and Pd(II). Ni(II) forms NiL_2Py_2 in the presence of

*LH = neutral ligand; L = monoanion

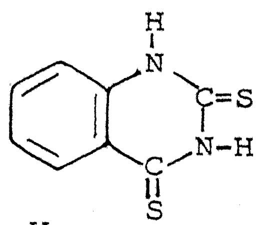


IV

$R = C_6H_5{}^a,\ CH_3{}^b,\ C_6H_3Cl_2{}^c,\ C_6H_4I^d,\ C_6H_4Cl^e,\ C_6H_5Br^f,$
$C_6H_4(CH_3)_2N^g$

pyridine. Shifts in four thioamide bands indicate that the ligands are bidentate, chelating through nitrogen and sulfur. These ligands have been found to be useful as analytical reagent for the gravimetric estimation of palladium and platinum. The ligand field parameters for Co(II) tetrahedral complexes are also reported. Cr(III) complexes[25] of the formula $[Cr(L)(CH_3COO)(OH)-H_2O].2H_2O$ with this class of ligands are postulated to have monomeric distorted octahedral structure. Monoanions of the thione are bidentate through nitrogen and sulfur. B' and 10 Dq have been calculated. In case of Cr(III) complexes for structure IV,R = C_6H_5, o-tolyl, p-chlorophenyl, p-methoxyphenyl.

Quinazoline(1H,3H)-2,4-dithione[26,27*]

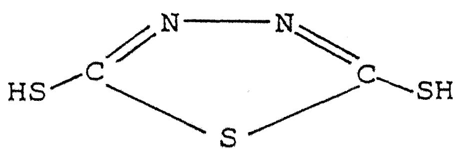


V

*LH_2 = neutral ligand; LH = monoanion; L = dianion.

The chelates of the type $Ni(LH)_2$, $Ni(LH)_2Py_2$, $Co(LH)_2$, $Co(LH)_2Py_2$, $Cd(LH)_2$, $Hg(LH)_2$, $Cu_2(L)(LH)_2$, $Ru(LH_2)(LH)Cl_2(H_2O)_2$, $Ru(LH_2)(LH)Cl_2(Py)_2$, $Ru(LH)_2(Py)_2$, $Rh(LH_2)(LH)Cl_2(H_2O)$, $Rh(LH_2)(LH)$-$Cl_2(Py)_2$, $[Rh(LH)_2Py]_2$, $[Rh(LH)_2(H_2O)]_2$ and $Rh(PPh_3)(LH_2)_2Cl$ have been reported. Shifts in the four thioamide bands and ν_{NH} in the complexes were utilized in deciding the donor sites. Appearance of new bands, i.e., ν_{M-N} and ν_{M-S} further confirmed the coordination sites. Based on u.v. and visible spectra and magnetic susceptibility data the stereochemistry of the complexes have been postulated. The ligand field parameters are also reported. The ligand is monodentate in the Rh(I), Ru(III) and Rh(III) complexes, bidentate in those of Rh(II) and Ru(II).

<u>1,3,4-Thiadiazole-2,5-dithiole[28*]</u>



VI

ML_2Cl (M = Ru, Rh), $RuL_2(H_2O)_2$, ML_2Cl_2 (M = Pd, Pt), IrL_3 complexes have been prepared and characterized on the basis of magnetic susceptibility electronic and infrared spectral data. Dq, B, β, C, f and h have been calculated. In all the cases coordination occurs through the thiol or thione sulfur of the ligand to different metal ions, and the complexes have an octahedral arrangement.

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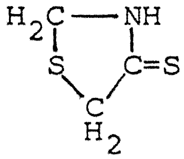
*LH = neutral ligand; L = monoanion.

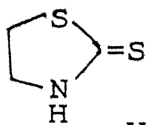
Thiazolidine-2-thione[29]*



VII

Compounds of the formulae ML_2 (M = Zn, Cd, Hg, Ni, Pd, Pt, Au). $ML_2.H_2O$ (M = Co, Mn), AgL, IrL_3 have been prepared and characterized on the basis of spectral and magnetic susceptibility data. Ligand field parameters Dq and B' have been evaluated by using the value of ν_2 and ν_3. These tetrahedral complexes are polymeric in nature. Ag(I) complex is linear and diamagnetic.

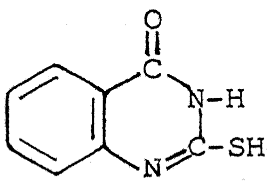
Tetrazoline-2-thione (ttz)[30]**



VIII

Complexes of the formulae $[Mn(ttz)_4Cl_2].4H_2O$, $[Mn(ttz)_2Br_2]$-$4H_2O$, $[Mn(ttz)_4I_2]\cdot[Mn(ttz)_2.SO_4].H_2O$, $[Mn(ttz)_4](BF_4)_2.2H_2O$, $[Mn(ttz)_4](ClO_4)_2.2H_2O][Mn(ttz)(OAc)_2].H_2O$ have been synthesized and characterized by means of spectral (i.r. and electronic) data. B and 10 Dq are also evaluated.

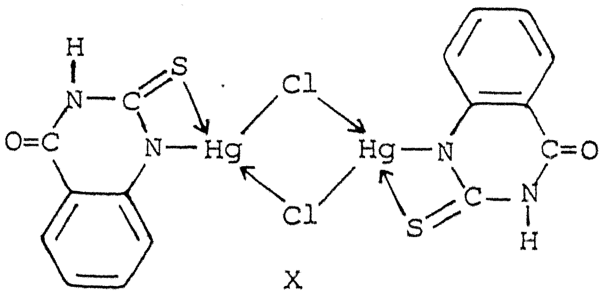
2-Mercaptoquinazole-4-one[31]***



IX

*L = monoanion; **ttz = neutral ligand; ***L = monoanion.

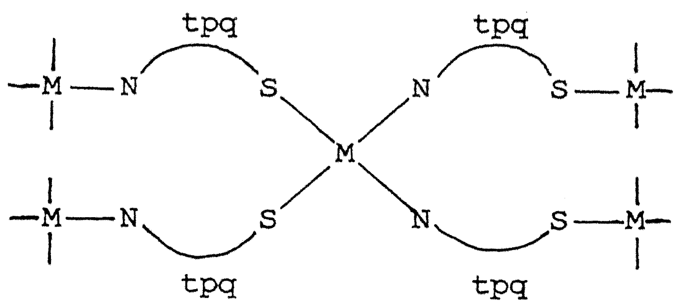
$[Co^{III}(L_2)Cl(H_2O)]$ has octahedral configuration. The ligand is simultaneously coordinated through N and S atoms. Dq and B' for the complex are found to be 1748 and 437 cm^{-1}, respectively. Diamagnetic tetrahedral complexes of the type ML_2 with Zn(II) and Cd(II) are formed, bonding sites being N and carbonyl oxygen. With Hg(II), dimer $[HgLCl]_2$ is formed which has the following structure:



X

A number of transition and non-transition metal complexes of 2-thione-3-(unsubstituted)-4-quinazolinone have been reported[31-35] but the ligating behaviour of 2-thione-3-phenyl-4-quinazolinone (Htpq) has not been much studied. Dave and coworkers[36] reported the Cu(II) and Ni(II) complexes of Htpq. Extensive work on ligating properties of Htpq has been carried out in our laboratory[37-39] which includes the reactions of the ligand (Htpq) with Co(II), Ni(II), Pd(II), Pt(II), Pt(IV), Mn(II), Ru(III) and Rh(III) in the presence and absence of various N-heterocyclic bases such as pyridine, β-picoline, o-phenanthroline, 2,2'-bipyridine, imidazole, pyrazole and pyrimidine in alkaline (pH $\simeq$ 9-10) medium.

The i.r. spectra of the Co(II), Ni(II), Pd(II), Pt(II), Pt(IV) and Ru(III) complexes indicate that Htpq is coordinated as anion through its exocyclic sulfur and imino-nitrogen atoms simultaneously. While the reactions of Htpq with Mn(II) salt in the presence and absence of bases led to the formation of oxo-manganese complexes. The presence of ν_{NH} of Htpq in oxo-manganese complexes indicate that the Htpq is coordinated as in its zwitterionic form. Both Mn(II) and Ru(III) complexes of Htpq were subjected to e.s.r. studies. These sparingly soluble complexes (except Ru(III) complexes) were proposed to have polymeric open (non-chelated) following structure:



XI

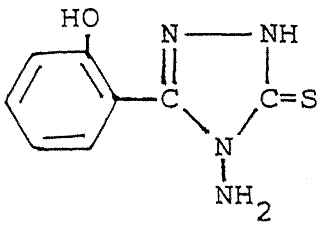
<u>2H-1,2,4-Triazole-3-thiol[40]*</u>

Complexes of the formulae $CoL_2(H_2O)_3$, $CoL'(H_2O)_3$, $NiL_2(H_2O)_3$, $Cu_2L_x(LH)_y(H_2O)_4$ (x + y = 2), $RhL_2(LH)$, $RhL_2(H_2O)_2$, PdL_2, $Pt(LH)_4Cl_2$ and AuL have been prepared. 10 Dq, B, β are also calculated. $NiL_2(H_2O)_3$, $CoL_2(H_2O)_3$, $CoL(H_2O)_3$, $RhL_3(H_2O)_2$, RuL_3 and $CuL(H_2O)_2$ are octahedral with bonding through thiocarbonyl sulfur and -NH nitrogen. PdL_2 is found to be square planar, bonding through

*LH = neutral ligand; L = monoanion; L' = dianion

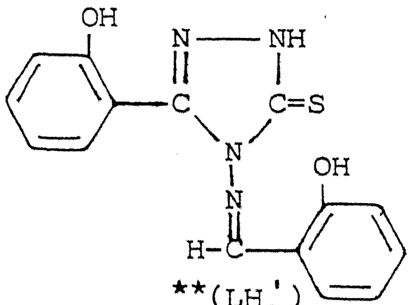
thiocarbonyl sulfur and -NH nitrogen after deprotonation. PtL_4Cl_2 is square planar and has the bonding through thiocarbonyl sulfur. The complex AuL is linear with bonding through thiocarbonyl sulfur and -NH nitrogen after deprotonation.

Triazoline thiones[41]



*(LH)

XII



**(LH_2')

XIII

Chelates of formulae ML_3 (M = Ru, Rh), ML'LH' (M = Ru, Rh), ML_2 (M = Pd, Pt), $M^{II}L'.H_2O$ (M = Pd, Pt) and $Pt^{IV}L_2'$ have been synthesized. 10 Dq, B and C have been evaluated. Compounds possess pseudooctahedral geometry. Ligand 3-(o-hydroxyphenyl)-1,2,4-triazoline-5-thione acts as a NS bidentate chelating agent coordinating via sulfur and hydrazine nitrogen atoms, whereas 3-(o-hydroxyphenyl)-4-(o-hydroxybenzylidine)-1,2,4-triazoline-5-thione acts as tridentate chelating agent having coordination sites at sulfur, azomethene nitrogen and phenolic oxygen.

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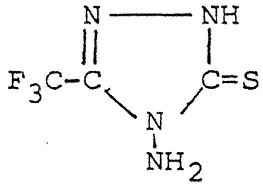
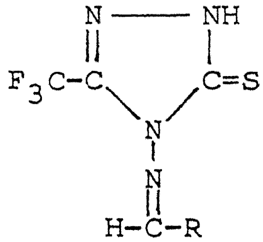
* LH = neutral ligand; L = monoanion.

**LH_2'= neutral ligand; LH' = monoanion; L' = dianion.

Triazoline thione[42]*



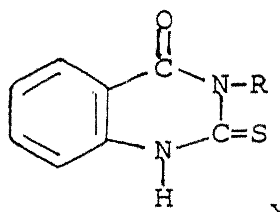
XIV



XV

R = $C_6H_5OH^a$, $C_4H_3O^b$, $C_6H_4OH^c$

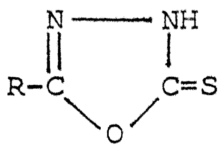
Quinazolone thione*



XVI

R = $CH_3{}^a$, $C_6H_5{}^b$, $C_6H_4{}^c$, $CH_3(o)^d$

Oxadiazole thione*



XVII

R = $C_6H_5{}^a$, $C_6H_4NO_2(p)^b$, $C_6H_4Cl(o)^c$

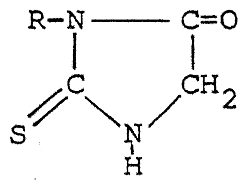
Twentyeight complexes of the formulae $CpTiCl_2L$, $CpTiClL_2$ and $CpTiL_3$ have been synthesized in dry dichloromethane medium.

---

*L = monoanion.

Triazoline thione ligand (3-trifluoromethyl-4-amino-1,2,4-triazoline-5-thione) acts as monobasic bidentate ligand having coordination sites at thiol sulfur and amino nitrogen, ligands (3-trifluoromethyl-4-benzylidine-1,2,4-triazoline-5-thione and 3-trifluoromethyl-4-furylidene-1,2,4-triazoline-5-thione) coordinating through thiol sulfur and azomethene nitrogen and the ligand (3-trifluoromethyl-4-salicylidene-1,2,4-triazoline-5-thione) behaves as dibasic tridentate ligand coordinating through thiol sulfur, phenolic oxygen and azomethene nitrogen, 3-substituted quinazole-4-one-2-thiones act as bidentate chelating agents, coordinating through thione sulfur and amino nitrogen (after deprotonation). Same type of coordination modes are postulated for oxadiazole thione derivatives.

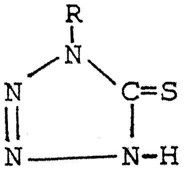
1-Aryl-2-thiohydantoin[43]



XVIII

R = C_6H_5 [a], $C_6H_4CH_3$ [b], $C_6H_5CH_2$ [c], $C_6H_4CH_3O$-p [d], $C_6H_4CH_3O$-o [e], $C_{10}H_7$ [f].

1-Substituted tetrazoline-5-thione[43]

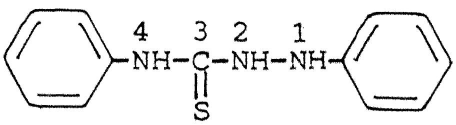


XIX

R = C_6H_5 [a], C_6H_4 [b], CH_3O-p [c], C_6H_4Cl-p [d], $C_6H_4CH_3$-o [e]

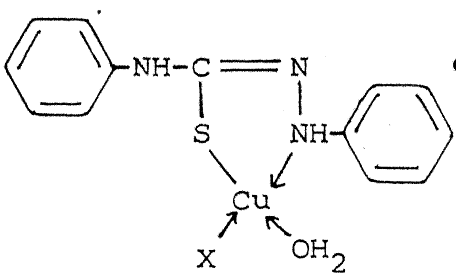
Complexes of formulae $CpTiCl_2L$, $CpTiClL_2$ and $CpTiL_3$ have been synthesized. Heterocyclic thioketones are bidentate through amino nitrogen and thione sulfur. The coordination modes have been decided on the basis of disappearance of ν_{NH}, δ_{NH} and red shift of thioamide III and IV bands after complexation. ^{1}H NMR spectra show a low field shift of the resonance signals of various protons in these complexes. One sharp signal at δ 4.8-4.9 ppm due to the NH proton disappears in the corresponding complexes.

1-Phenyl 1,4-diphenylthiosemicarbazide[44]

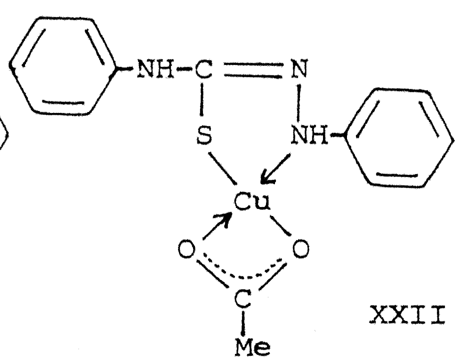


XX

Cu(II), Co(II), Hg(II) complexes have been prepared and characterized. The i.r. spectral studies have been used to determine the bonding sites and the following structures have been suggested:

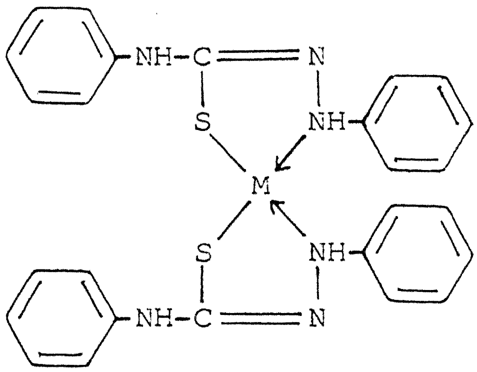


XXI



XXII

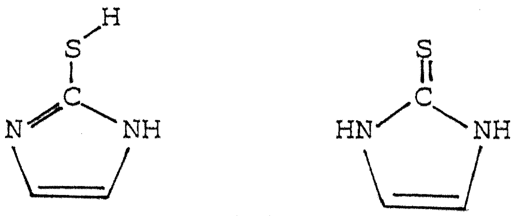
X = Cl or Br



M = Co(II), Hg(II)

XXIII

Imidazoline(1,3H)-2-thione[45]

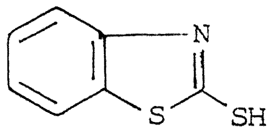


XXIV

Co(II) and Zn(II) complexes have distorted octahedral structures. The ligand functions as a chelate through nitrogen and sulfur or is unidentate through sulfur only. Of the four thioamide bands those showing the most significant changes upon coordination are I & IV. Thioamide band I ($\nu_{CN} + \delta_{CH}$) shows negative shifts ranging from 25-50 cm^{-1}. Thioamide band IV has its greater contribution from $\nu_{C\text{---}S}$ and this band also exhibits negative shifts. These observations are consistent with coordination of the metal with both N and S atoms of this ligand. ML_2X_2 (M = Co, Zn; X = Cl, Br, I), ML_4X_2 (M = Co, Zn; X = NO_3, ClO_4) have been synthesized and characterized.

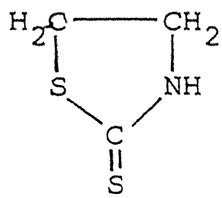
For Ni(II) complexes[46] thioamide bands I & IV were found inconclusive to differentiate between M-N and M-S contacts.

2-Mercaptobenzothiazole[47]*

XXV 

Livingstone and coworkers have reported the synthesis and characterization of the metal complexes (ML_2) (M = Ni , Pd, Pt, Zn, Cd) AgL and CuL.LH of 2-mercaptobenzothiazole (LH). The i.r. evidence indicates that the ligand is chelating NS donor, AgL is reported to have polymeric structures. No definitive structure of Cu complex could be found.

1,3-Thiazolidine-2-thione (tzz)[48]**

 XXVI

$Cu(tzz)_2Cl_2$ is non-conducting in nitromethane. The ligand is bonded to the metal through the thioketonic sulfur atom, as shown by the shifts of the ν(CN) + δ(NH) and of the ν(C=S) b~~o~~ands. In fact, the thioamide I (ν(CN) + δ(NH)) band, present in the free ligand at 1510 cm^{-1} is shifted to higher frequencies (1530 cm^{-1}) and ν(C=S) undergoes a downward shift, indicating an increase in the double bond character of the CN linkage and co-ordination through thioketonic sulfur. For N-coordination the opposite changes in these vibrational modes are expected.

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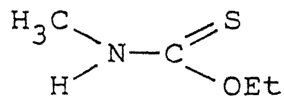
*LH = neutral ligand; L = monoanion

**tzz = neutral ligand.

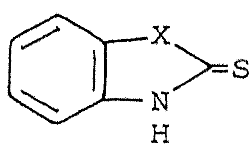
2-Methyl-O-ethylthiocarbamate[49] (MTC)*



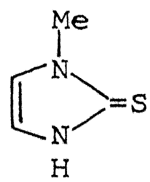
XXVII

Rhodium(III) halide complexes with N-methyl-O-ethylthiocarbamate [Rh(MTC)$_3$X$_3$] (X = Cl, Br, I) show coordination through the sulfur atom. The free MTC absorption at 1535 cm^{-1} assigned as mainly ν(C$\cdots$N) with a small ν(NH) contribution in accordance with analogous thioamides[50,51] displaced towards higher energies on coordination. In complexes of analogous geometry for instance trans-[M(MTC)$_2$X$_2$] (M = Pd, Pt; X = Cl, Br, I), the shift depends on the halide in the order Cl$>$Br$>$I.[52,53] A halide dependent upward shift of thioamide I ($\nu_{C\cdots N}$ + δ_{NH}) is clearly observed in the 1:3 rhodium adducts.

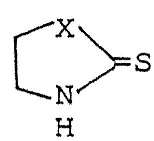
Heterocyclic thioamides[54]



X = O, S, NH



XXVIII

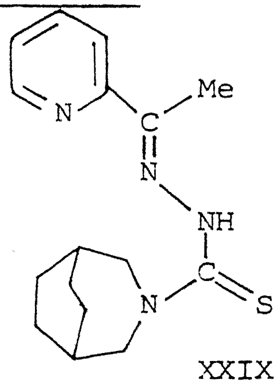


X = S or NH

The reaction of [Os$_3$(CO)$_{10}$(MeCN)$_2$] with the heterocyclic thioamides yields products which are formulated as [Os$_3$H(CO)$_{10}$L] (L being the deprotonated thioamide coordinated via the exocyclic sulfur atom). The structure of [Os$_3$H(CO)$_{10}$(SC=NCH$_2$CH$_2$S)] has been established by X-ray analysis.

*MTC = neutral ligand

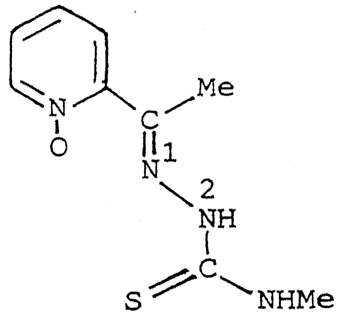
3-Azabicyclo[3.2.2]nonane-3-thiocarboxylic acid 2-[1-(2-pyridinyl)ethylene]hydrazide[55]*



XXIX

(LH) and its selenium analogue (HLSe) have been used to prepare [NiLX] (X = Cl, Br, NCS, N_3, NO_2 or NCSe) and [Ni(LSe)Cl]. These are diamagnetic planar complexes. A single crystal study of [NiL(NCS)] shows the deprotonated ligand bound in a tridentate manner via its pyridyl nitrogen, imine nitrogen and the thione sulfur atom with the nitrogen atom of the thiocyanato ligand occupying the fourth coordination position. [NiL_2] solid is octahedral with the two deprotonated ligands bonding as tridentate groups via same atoms as in the case of [NiLX] complexes. In [$Ni(HL)_2(H_2O)_2$]$(BF_4)_2$, [$Ni(HL)_2(NO_3)_2$ and [$Ni(HL)_2(H_2O)_2$].I_2, the neutral HL ligands are coordinated in a bidentate fashion via the pyridine and imine nitrogen atoms.

N-Methyl-2-[1-(2-pyridinyl-1-oxide)ethylidene]hydrazinecarbothioamide[56]



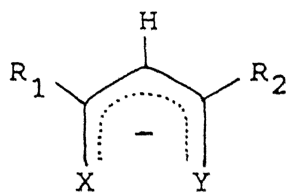
XXX

*LH = neutral ligand; L = monoanion.

Series of Co(III), Ni(II) and Cu(II) complexes have been prepared. The deprotonated ligand binds as tridentate via the N-oxide oxygen, the imine nitrogen (N^1) and the sulfur while the neutral ligand coordinates primarily as a bidentate ligand via only oxygen and imine nitrogen. It functions as a monodentate ligand via the N-oxide oxygen.

<u>Thio-β-diketones</u>

Holm and coworkers[57-60] have studied systematically the stereochemical and electronic effects of sulfur donor substitution in a variety of closely related chelate ligands of the type XXXI. By making comparisons among complexes identical in constitution except for the donor atom sets; the particular stereochemical consequences of sulfur ligation were assessed as follows:



XXXI

<u>XXXIa</u>, X = Y = O, β-diketone; <u>XXXIb</u>, X = O; Y = S, mono thio-β-diketone; <u>XXXIc</u>, X = O; Y = NR, β-ketoamine; <u>XXXId</u>, X = S; Y = NR, β-ketothione

(1) In general, unsaturated, sulfur containing chelate ligands may induce preferential stability of structures that are either unusual or of widespread occurrence. Thus, sulfur tends to stabilize the planar form of monomeric complexes,

particularly those of Ni(II) and Co(II). Examples include planar bisthiolene[61] complexes and monothio[62,63] and dithioacetylacetonates.[64,65] The trigonal prismatic structures of certain tris-dithiolenes are unique to sulfur chelates.[61]

In the case of nickel complexes of XXXIc and XXXId, measurements in non-coordinating solvents showed the presence of planar-tetrahedral equilibria.[57,60] However, the equilibrium positions are such that the population of the planar isomer of the β-aminothione complex XXXId is always considerably greater than that of the β-ketoamine member (XXXIc) of the same pair. Thermodynamic measurements of these complexes confirmed that sulfur effects greater stabilization of the planar stereochemistry than does oxygen and that the inequalities in stereochemical populations are due to enthalpy rather than entropy effects.[57] It was suggested that source of the stability differences of these isomers is associated with a larger extent of metal ligand π-bonding in the β-aminothiones which can occur via ligand → metal (HOMO → pz) and/or metal → ligand (d_{xz}^2, d_{yz}^2 → LUMO, sdπ) electron transfer superimposed on the related σ bond strengths.[57]

(2) For square planar monothio-β-diketone complexes of nickel(II), palladium(II) and platinum(II), structural data have shown that only the cis-isomer is formed.[66-71] Similarly, with the octahedral complexes of trivalent cobalt, vanadium, iron, ruthenium and rhodium, n.m.r. studies,[60] dipole moment measurements,[72,73] and X-ray results[74,75] all show that the cis (facial)

arrangement is adopted exclusively. This preferential stability of the cis form may arise in part from non-bonded S---S interactions in the S_2 or S_3 units similar to those that have been suggested to assist in the stabilization of trigonal prismatic coordination.[76]

(3) Another structural consequence is the depolymerization. Sterically unencumbered nickel(II) β-diketonates are trimeric in the solid state[77] and solution,[78] but similar NiO_2S_2,[62,63] $NiOS_3$[79] and NiS_4[65,79] complexes are without exception monomeric and planar in both phases. Similarly, polymeric[80] cobalt(II) β-diketonates are degraded to simple CoO_2S_2[58] and CoS_4[65,79] monomers upon sulfur substitution.

Introduction of sulfur into the metal coordination sphere also promotes spin pairing. For example , while tris (acetylacetonato)iron(III) [FeO_6] is high spin but the dithioanalog [FeS_6] is low spin.[81] In ferric monothio-β-diketonates [FeO_3S_3] exhibit spin isomerism to an extent dependent on the chelate ring substituents.[62,63] Donor atom dependence has also been observed in the n.m.r. spectra of thio-β-diketone complexes. Substitution of oxygen by sulfur causes a shift of both the methine and ring substituent proton resonance to lower field.[79]

The mass spectrometric behaviour of the isostructural series of nickel complexes, bis(dipivaloylmethanido)nickel(II), and the monothio and dithio analogs has been studied.[82] It was

observed that for the sequence $NiO_4 \rightarrow NiO_2S_2 \rightarrow NiS_4$, there was a marked decrease in the contribution of molecular ion peaks and, in general the percentage of the total ion current due to metal-containing peaks decreased in the order $NiO_4 > NiO_2S_2 > NiS_4$. The character of the spectra changed from one dominated by the fragmentation of the complexed ligands in NiO_4, to one dominated by fragmentation of the uncomplexed, oxidized ligands in NiS_4. This trend was observed in other similar complexes of both nickel and cobalt.[82]

A polarographic study[83] of above series of nickel complexes confirmed that substitution of oxygen by sulfur has both thermodynamic and kinetic consequences. As the number of sulfur atoms around the nickel atom increases, the reduction is easier (more positive $E_{1/2}$) and the heterogeneous electron transfer step is faster. This trend parallels that observed[84] for the ML_3 complexes of acetylacetone and dithioacetylacetone and for the NiLL' complexes of monothio and dithioacetylacetone.

The consequence of gradual replacement of oxygen by sulfur is thus well illustrated by the series of complexes formed from acetylacetone and its thioanalogs. The detailed informations regarding ligation of monothio-β-diketone,[62,63,85] dithio-β-diketone[86,87] and related ligands are given in various reviews.

Thiocarbamates

(i) Monothiocarbamates

The related dithiocarbamates have been under study for well over seventy years whereas the coordination chemistry of monothiocarbamate ligands has received attention only during the past ten years.

The most common synthetic procedure for N,N-disubstituted monothiocarbamate ligand involves the treatment of carbonyl sulfide OCS with a secondary amine to provide a salt[88-90] as shown in the equation:

$$2\ R_2NH + OCS \longrightarrow [R_2NH_2]^+\ [R_2NCOS]^-$$

The majority of the studies have involved the following secondary amines: N,N-dimethylamine; N,N-diethylamine; N,N-dipropylamine; piperidine; pyrrolidine; indole; pyrrole and indoline. In general, the ammonium and alkali metal salts provide reasonable stable starting materials (when dry) for the synthesis of a wide variety of metal complexes.

Most of the complexes reported to-date have been prepared by metathetical reaction of a monothiocarbamate salt with transition metal salt in a polar non-aqueous solvent. All the complexes reported thus far involve ligands of the type: $R_2NC(=O)S^-$ $(R \neq H)$. Metal dialkylamides have been shown[91,92] to form monothiocarbamates

when treated with OCS presumably is an insertion reaction:

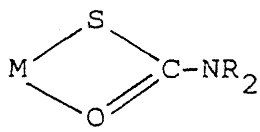
$$M(NR_2)_4 + 4\ OCS \longrightarrow M(OCSNR_2)_4$$

M = Th, U, Ti, Zr and R = Me, Et, i-Bu

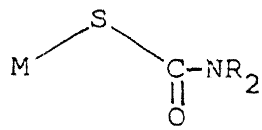
A unique and interesting procedure for the synthesis of $Fe(Me_2mtc)_3$ has been reported by Nakajuma and coworkers.[93] Bis-(N,N-dimethylcarbamoyl)-disulfide was reacted with $Fe_2(CO)_9$ to give what was thought to be $[Fe(Me_2mtc)_2]_n$ as an insoluble polymeric material. Oxidation of this material with elemental S or Se provided $Fe(Me_2mtc)_3$. Finally, the tin derivatives $Me_3Sn(R_2mtc)$ have been used as a starting material[94] for several organometallic complexes, as illustrated by the reaction:

$$Me_3Sn(R_2mtc) + Mn(CO)_5Br \longrightarrow Mn(CO)_5(R_2mtc) + Me_3SnBr$$

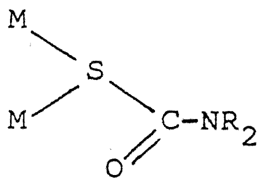
A few examples of well characterized complexes are $[Cu(Pr_2mtc)]_6$,[95] $[Zn(pipmtc)_2(pip)_2]$,[96,97] (pip = piperidine), $Ti(Et_2mtc)_4$,[98] $(\eta^5-C_5H_5)[Mn(CO)_3Me_2mtc)_2]$,[94] $(\eta^5-C_5H_5)Mo(CO)_2(Me_2mtc)$,[99] $Fe(Me_2mtc)_3$,[100] $[Co(pyrmtc)_2(pyr)_2]$[101] (pyr = pyrrolidine), $[Ni(R_2mtc)_2]_6$,[102] $[Pd(R_2dtc)(R_2mtc)]_2$, $[\eta^5-C_5H_5)_2U(Et_2mtc)_2$,[103] and $Rh(MTC)_3Cl_3$ (MTC = N-methyl-O-ethylthiocarbamate). The structural studies reported todate unequivocally establish that there are at least four bonding modes for monothiocarbamate ligands, shown below:



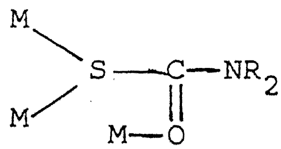
XXXII



XXXIII

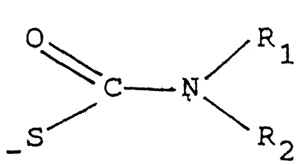


XXXIV

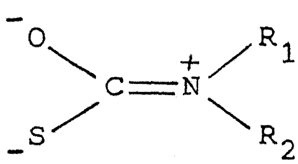


XXXV

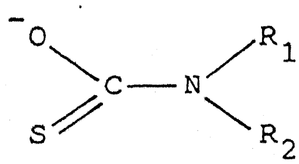
The monothiocarbamate ligand is bonded monodentately through sulfur to soft metal ions whereas it is bidentate to hard acids.[104] In all the reported structures the sulfur atom of the ligands are located cis. The appearance of $\nu(C \cdots N)$ above 1545 cm^{-1} has been taken to indicate that the ligand is bonded monodentately through sulfur, values below 1545 cm^{-1} are considered to be characteristic of bidentate ligands. There are exceptions and structural inferences based solely upon i.r. data must be viewed with caution. I.r., n.m.r. spectral data and X-ray structural studies are indicative of the relative importance of canonical form XXXVII in the valence bond description of the electronic structure of monothiocarbamate ligands:



XXXVI



XXXVII



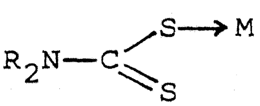
XXXVIII

The relative importance of canonical forms XXXV and XXXVII is difficult to assess. Based on electronegativity argument one would expect XXXVII with negative charge residing on oxygen, to be more important than XXXVI, with negative charge residing on sulfur. However, the chemical properties particularly the tendency of the sulfur moiety to bridge, suggest that the sulfur donor has considerable "mercaptide" character, consistent with form XXXVI.

Recently[105] some new organocobaloxime derivatives have been synthesized by reaction of pyridine bis(dimethylglyoximato)-cobalt(II) with S-vinylmonothiocarbamates under H_2, in which (N,N-disubstituted) S-vinylmonothiocarbamates are attached to the Co atom via a Co-C σ bond. The chemistry of monothiocarbamates has been recently reviewed by McCormic and coworkers.[106]

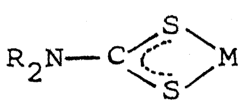
(ii) Dithiocarbamate

These complexes have been extensively studied and some of them are commercially used as fungicides. Dithiocarbamates and their analogues have two potential sulfur donor atoms joined to a single C-atom and their complexes are, some time, called 1,1-dithiolato complexes. The bonding of dithiocarbamates is variable and can function either as unidentate or bidentate (chelating) ligand.



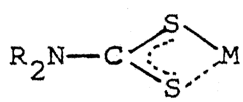
Unidentate

XXXIX



Symmetrical chelate

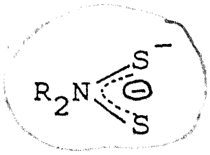
XL



Unsymmetrical chelate

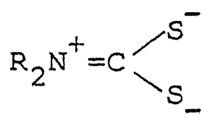
IXL

The unidentate and chelate types can be distinguished by i.r. and n.m.r. spectra.[107] The n.m.r. spectra of chelate dithiocarbamate groups are commonly temperature dependent due to dynamic processes involving nonequivalence of the R groups, rotation about the C-N bond, and for tris-chelates $M(dtc)_3$, intramolecular metal centred dynamic processes by a trigonal twist mechanism.[108] In chelating mode they frequently stabilize the metal centre in an unusually high apparent formal oxidation states, e.g., $[Fe^{IV}(S_2CNR_2)_3]^+$ and $[Ni^{IV}(S_2CNR_2)_3]^+$. They also have propensity for stabilizing novel stereochemical configurations, unusual mixed oxidation states, intermediate spin states (e.g., Fe(III), S = 3/2) and for forming a variety of tris-chelated complexes of Fe(III) which lie at the $^3T_1 \rightarrow {}^6A_1$ spin cross over.[109] The major forms for dithiocarbamate are:



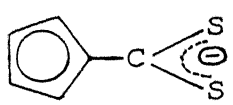
VIIIL

and



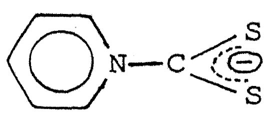
VIIL

The NR_2 group has a strong electron releasing effect and when this is altered as in ligands such as



VIL

and



VL

are different behaviour towards metal can be achieved.[110,111] Thus, in the cyclopentadienyl compound, the driving force tending

to make the ring aromatic leads to a dominant π-acceptor character at sulfur.

The metal dithiocarbamates have been reviewed by Coucouvanis,[112] Eisenberg[113] and Burns and coworkers.[114] These reviews present a comprehensive account of the work reported in the literature. There is however, continuous interest in the synthesis, characterization, electronic structure and bonding of these complexes. A few selected recently reports are cited below.

Templeton and coworkers[115] reported a series of seven coordinate $M(CO)_{3-n}L_n(S_2CNC_4H_4)_2$ (n = 0-2) molybdenum(II) and tungsten(II) complexes with electronically unique pyrrole-N-carbodithioate chelating ligand: [$M(CO)_2L(S_2CNC_4H_4)_2$: M = Mo, W; L = PPh_3, PEt_3, $P(OMe)_3$; M = Mo; L = OC_4H_8, $AsPh_3$, $SbPh_3$, SC_4H_8; $M(CO)L_2(S_2CNC_4H_4)$; M = Mo, W; L = $P(OMe)_3$; M = Mo; L = PEt_3, 1/2 $Ph_2PCH_2CHPCH_2$; $[R_4N]$-$[M(CO)_2X(S_2CNC_4H_4)_2]$: M = Mo, W; X = F; M = Mo; X = Cl, Br, I].

$[M(RC{\equiv}CR)_2(S_2CNMe_2)]$[116] (M = Mo or W), $[W(PhC_2H)_3(S_2CNMe_2)_2]$[117] and $[Fe(S_2CNR_2)XX']$[118] have recently been reported.

The syntheses, spectral properties and substitution reactions of $M(CO)_3(S_2CNC_4H_4)_2$ (M = Mo, W) have been carried out.[119] Jasmine and coworkers[120] have reported the X-ray crystal structure of $[Mo((C_2H_5)_2NCS)_4](Cl.H_2O).XCHCl_3$ (X = 0.88). In the eight coordinated niobium(V) and tantalum(V) N,N-disubstituted dithiocarbamates and monothiocarbamates, the metal-centred rearrangements and its stereochemistry are discussed.[121] The diethyldithiocarbamates

interaction with n-type cadmium sulfide and cadmium selenide in $CH_3CN/0.2$ M $NaClO_4$ has been reported recently.[122] Baired and co-workers[123] have studied the reactivity and crystal and molecular structure of oxo-bis(diethylcarbamodidithiato)(tetrahydrofuran)-iodoxamolybdenum(V)

Thiobiuret

$RHN-\underset{\underset{X}{\|}}{C}-NH-\underset{\underset{X}{\|}}{C}-NHR'$ (R,R' substituents; X = O/S)

IVL

ML_2Cl_2 type of complexes (L = $NH_2CONHCSNH_2$); (M = Co(II), Ni(II), Cd(II), Hg(II)) have been synthesized and their structures have been proposed on the basis of spectral (i.r. and electronic) and magnetic studies. The ligand is bidentate in Ni(trans-octahedral) and Cd(tetrahedral) complexes. In tetrahedral complexes of Co(II) and Hg(II), the ligand is unidentate.[124] Vanadyl(V) chloride forms $VOCl_3L$ with 1,5-disubstituted-2-thiobiuret(=L) in CCl_4 solution. The ligand is bidentate through its S and O atoms.[125]

Many complexes of dithiobiuret and substituted dithiobiuret are known.[126-131] The complexes of Zn(II), Ni(II), Sn(II) and Cu(II) with substituted dithiobiuret (R = R' = Me, Et, morpholine) have been found[132] to be useful in population control as insectisides and those of Ag(I), Cu(I), Ni(II), Pd(II), Hg(II), Fe(III), Zn(II), Cd(II), Cu(II), and Co(II)[133-137] with substituted dithiobiuret (R = Ph; R' = o-MeC_6H_4, p-MeC_6H_4; R = Me, R' = o-MeC_6H_4,

p-MeC_6H_4) as fungicides. A few additional compounds[138-140] of $Ni(NH2CSNHCSNH_2)_2X_2$ (X = Cl, Br, I, $\frac{1}{2}SO_4$, CH_3CO) have also been isolated. The crystal structures[141] of the two of the additional compounds $Ni(NH_2CSNHCSNH_2)_2$glycol, $Ni(NH_2CSNHCSNH_2)_2(ClO_4)_2.EtOH$ have been determined to investigate: (a) the class of metal-ligand in neutral complex, (b) structural differences between neutral ligand complex and uninegative complex and (c) the hydrogen bonded system in cationic complex.

The vanadium[142] dithiobiuret complex, $[(Cp)_2V(NH_2CSNHCSNH_2)]$-$[PF_6]$ (Cp = η^5-C_5H_5), has been reported and pseudotetrahedral structure has been assigned on the basis of i.r., magnetic susceptibility, e.s.r., electronic spectra and molar conductance studies.

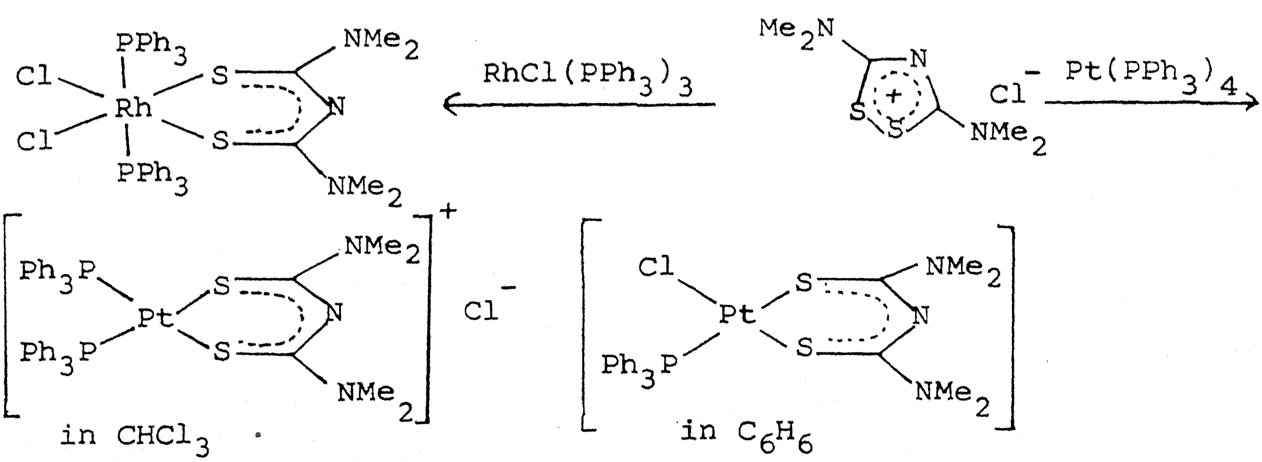
Gal and coworkers[143] reported the Rh and Pt complexes of dithiobiuret of general formulae: $Rh(CO)(PPh_3)L$, $Rh(PPh_3)_2L$ and $PtH(PPh_3)L$ (L is bidentate and coordinated through both S atoms). These complexes undergo reaction with oxygen giving 1:1 dioxygen adduct. In solution trans product of the complex, $Rh(PPh_3)_2(O_2)L$ has been observed. Pignedoli and coworkers[144,145] have prepared and characterized number of 2,4-dithiobiuret (L) complexes of Zn(II), Cd(II) and Cu(I). In the complexes $Cd_2L_3Cl_4$, CdL_2X_2 (X = Br, I, ClO_4), $CdL_4(NO_3)_2$ and $CdL_3(SO_4).H_2O$, ligand is monodentate and coordinated through one S atom, with a possible secondary weaker interaction of other CS group. The halide complexes were found non-conducting with bridging halide ligands while perchlorate complex in DMF is a 1:2 electrolyte. The

nitrate and sulfate complexes are insoluble in DMF and probably have coordinated anions. CuLX (X = Cl, Br, I)[146] have been synthesized and characterized.

Sukhoruchkina and coworkers[147] studied the complexation of Cu(I) and Cu(II) with 2,4-dithiobiuret to determine the mechanism for Cu(II) catalysis of redox reactions between metal ions and 2,4-dithiobiuret (BH). Amphoteric, potentiomeric and spectrophotometric studies indicate the formation of CuBCl at 1:1 Cu:HB ratio, but at 1:1.5 ratio, a redox reaction occurs, giving CuCl and the corresponding dithiazolidine. The dithiazolidine then forms a 1:2 Cu(I):ligand complex. Recently,[148] Raman and i.r. spectra of 2,4-dithiobiuret (L), CuL_2Cl_2 and their deuterated derivatives were studied extensively by Jennings and coworkers.

Tetramethyldithiobiuret ($Me_2NCSNHCSNMe_2$ = L) reacts with[149] $Mo(CO)_3(\eta^5-C_5H_5)Cl$ in the presence of Et_3N to give the complex $[Mo(CO)_2(\eta^5-C_5H_5)(L)]$ with six membered ring.

The oxidative addition of unsaturated cyclic five membered disulfides to $RhCl(PPh_3)_3$ and $Pt(PPh_3)_4$ resulted in the formation of corresponding dithiobiuret complexes as given below:[150]



The reaction with $Pt(PPh_3)_4$ was found to be solvent dependent.

Mn(II) dithiobiuret complexes,[151] MnL_2SO_4 and $MnL_2X_2.EtOH$ (X = NCS, OAc) were prepared and characterized by i.r. spectra and thermal analyses. The ligand is bidentate with coordination through both S atoms, thus making the complexes octahedral, the sulfate group is in inner sphere whereas one of each OAc and NCS group is in outer sphere and other one is in bridging form.

Recently, Fe(III) complexes of substituted dithiobiuret, $(FeCl_3L)_n$ (n = 1,2; L = RNHCSNHCSNHR'; R = R' = Ph, o-, p-tolyl; R = Ph, R' = o-, p-tolyl), have been reported. The dielectric constant and resistivity of these characterized complexes were studied as function of temperature. The data indicate possible transition at 90 and 185^{o} for monomers whereas dimers show no peaks.[152]

Aromatic Thioamides

The aromatic thioamides (ArCSNHCOR) (Ar = 2-pyrrole, 2-thiophene; R = OEt, NHPh, NH_2) and thiocarboximides such as 2-thiopyrrole-1,2-dicarboximide and pyrrole-1,2-dithiocarboximide have been synthesized by E.P. Papadopolous in 1973-74. These monothio-β-diketone type ligands can function either as neutral or as anions with N, S and O as potential donors. Obviously their simultaneous participation in the complex formation would be virtually impossible. A study of the metal complexes of

N-ethoxycarbonylpyrrole-2-thiocarboxamide (ETH), N-phenylcarbamoylpyrrole-2-thiocarboxamide (PTH), N-carbamoylpyrrole-2-thiocarboxamide (CPTH), 2-thiopyrrole-1,2-dicarboximide (TPH)[153-155] and pyrrole-1,2-dithiocarboximide (PDD)[156] have been carried out to correlate the different physiochemical properties of the various metal complexes. Thus the monomeric forms of the complexes of ETH and PTH with the metal ions Co(II), Ni(II), Cu(I), Cu(II), Ag(I), Zn(II), Cd(II), Pt(II), Pt(IV), Pd(II), Rh(I), Rh(III), Ru(II), Ru(III) and Au(III), complexes of CPTH and TPH with Cu(I), Cu(II), Ag(I), Co(II), Ni(II), Ru(II), Rh(I), Pd(II) and Pt(II), Complexes of N-ethoxycarbonylthiophene-2-thiocarboxamide (ETH) with Cu(II), Ni(II), Ag(I), Ru(III), Rh(III), Rh(I), Pd(II) and Pt(II),[157] Complexes of PDD with Fe(II), Ru(II), Rh(I), Ni(0), Pd(0), Co(I), Pt(0), Cu(I), Ag(I) have been proposed.

The rare occurrence of Co(II) diamagnetic complexes with the pyrrole derivatives as ligand have been explained by the possible formation of δ-bond between two Co(II) ions present in the square planar geometry. Different modes of bonding with these ligands have been reported. The ligating behaviour of these thiocarboxa(i)mides can be summarized as follows:

i) can function as neutral bidentate chelating ligands,

ii) may function as neutral monodentate or anionic ligand,

iii) can function as bidentate or tridentate to two metal ions.

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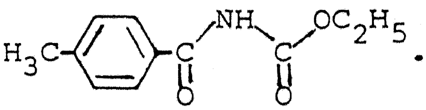
CHAPTER II

TRANSITION METAL COMPLEXES OF N-CARBOETHOXY-4-TOLUENETHIOAMIDE: SULFUR ABSTRACTION FROM N-CARBOETHOXY-4-TOLUENETHIOAMIDE BY Ag(I), Cu(II), Pb(II), Hg(II) AND Cd(II) IONS*

This chapter describes the reaction of N-carboethoxy-4-toluenethioamide (Hctt) with a variety of transition metal ions leading to the formation of M(II)(ctt)$_2$ (M = Ni, Co, Cu, Ru, Pd and Pt). Ru(III) and Rh(III) form Ru(ctt)$_3$ and Rh(ctt)(Hctt)Cl$_2$ whereas Co(II) and Ni(II) in presence of pyridine give M(II)-(ctt)$_2$py (M = Ni and Co). [Rh^{I}Cl(PPh$_3$)$_3$], [Pd^{0}(PPh$_3$)$_4$] and [Pt^{0}(PPh$_3$)$_4$] react with Hctt to yield [Rh^{I}Cl(Hctt)$_2$(PPh$_3$)], [Pd^{0}(Hctt)$_2$(PPh$_3$)$_2$] and [Pt^{0}(Hctt)$_2$(PPh$_3$)$_2$], respectively.

Reaction of Hctt with soft metal ions under reflux conditions yields metal sulfide and the oxygenated form of the ligand:



. The reaction products have been characterized on the basis of chemical analyses, conductivity, spectroscopic and magnetic measurements studies.

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*Synth. React. Inorg. Met. Org. Chem., 16(10), 1435 (1986).
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II.1 EXPERIMENTAL

All the chemicals used were chemically pure. The ligand (Hctt) was prepared by known procedure (see Appendix). Copper, cobalt, nickel, palladium, platinum, phosphorus, sulfur and chloride were determined gravimetrically. Analyses of C, H, N were done at the Microanalytical Laboratory, I.I.T., Kanpur. The I.R. spectra of the ligand and complexes were recorded as KBr pelletes in the range 4000-250 cm^{-1}. The electronic spectra were recorded on a Cary Model-17D UV-Visible spectrophotometer. Magnetic susceptibilities of the complexes at room temperature (298 ^{o}K) were determined by using a parallel field vibrating sample magnetometer (VSM) model 150A.

II.1.1 Preparation of the Complexes

(i) Bis(N-carboethoxy-4-toluenethioamidato)nickel(II)

A cold solution of Hctt (0.45 g, 2 mmol) in ethanol (10 ml) was added dropwise to the solution of $NiCl_2.6H_2O$ (0.25 g, 1 mmol) containing pyridine (2-3 ml) in H_2O (30 ml). The brown precipitate thus obtained was filtered, washed with H_2O and dried at 110^{o}C.

(ii) Bis(N-carboethoxy-4-toluenethioamidato)monopyridine-nickel(II)

This complex was obtained by the procedure described exactly as in (i) except that the 10–15 ml of pyridine was used in place of 2-3 ml.

(iii) Bis(N-carboethoxy-4-toluenethioamidato)cobalt(II)

An aqueous solution (25 ml) of $[Co(NH_3)_6]Cl_3$ (0.26 g, 1 mmol) was treated with an ethanolic solution of the ligand, Hctt (0.45 g, 2 mmol). The reaction mixture was stirred for 3-4 hrs. The black brown precipitate thus obtained was filtered, washed with H_2O, ethanol and diethyl ether and dried *in vacuo*.

(iv) Bis(N-carboethoxy-4-toluenethioamidato)monopyridine-cobalt(II)

A cold solution of Hctt (0.45 g, 2 mmol) in ethanol (10 ml) was added dropwise to a stirred and an ice-cold solution of $CoCl_2.6H_2O$ (0.25 g, 1 mmol) in H_2O (30 ml) containing pyridine (15 ml) under nitrogen atmosphere. The reaction mixture was stirred for 0.5 hr. The dark-green precipitate thus obtained was filtered, washed with cold water and dried *in vacuo*.

(v) Bis(N-carboethoxy-4-toluenethioamidato)copper(II)

An aqueous solution (25 ml) of $CuCl_2.2H_2O$ (0.17 g, 1 mmol) was mixed with an ethanolic solution (10 ml) of the ligand (0.45 g, 2 mmol). The brown precipitate so obtained was digested on a water bath for half an hour, filtered, washed with water, ethanol, ether and dried in *vacuo*.

(vi) Tris(N-carboethoxy-4-toluenethioamidato)ruthenium(III)

To a stirring solution of $RuCl_3.3H_2O$ (0.21 g, 1 mmol) in ethanol (15 ml) (warmed at 60^oC) was added an ethanolic solution

(5 ml) of ligand, Hctt (0.66 g, *ca*. 3 mmol). Refluxed the reaction mixture for 2 hrs, the black precipitate thus obtained was filtered, washed with ethanol, diethyl ether and dried *in vacuo*.

(vii) Bis(N-carboethoxy-4-toluenethioamidato)ruthenium(II)

$RuCl_3.3H_2O$ (0.21 g, 1 mmol) in THF (20 ml) ligand Hctt (0.045 g, 2 mmol) and Zn dust (0.038 g, 0.58 mmol) were heated for an hour. The reaction became intense violet, evaporated, extracted with $CHCl_3$, recrystallised from CH_2Cl_2 petroleum ether and dried *in vacuo*.

(viii) Dichloro(N-carboethoxy-4-toluenethioamidato)(N-carboethoxy-4-toluenethioamide)rhodium(III)

An ethanolic solution (40 ml) of $RhCl_3.3H_2O$ (0.1 g, 0.5 mmol) and Hctt (0.23 g, 1 mmol) was concentrated on a water bath to about 10 ml,added water to precipitate reddish brown complex, filtered, washed with water and dried at 110°C.

ix) Bis(N-carboethoxy-4-toluenethioamidato)palladium(II)

$PdCl_2$ (0.18 g, 1 mmol) in dil. HCl (25 ml) was added to an ethanolic solution (25 ml) of the ligand (0.45 g, 2 mmol). The reaction mixture was stirred for 5 minutes. The yellowish brown complex, thus obtained was filtered, washed with dil. HCl (10^{-3} M), distilled water, ethanol, ether and dried *in vacuo*.

(x) Bis(N-carboethoxy-4-toluenethioamidato)platinum(II)

The ethanolic solution (5 ml) of the ligand Hctt (0.45 g, 2 mmol) was mixed with a warm aqueous solution (20 ml) of K_2PtCl_4 (0.41 g, 1 mmol), refluxed for 0.5 hr. The brown precipitate thus obtained was digested for 0.5 hr on a water bath, filtered, washed with hot water, and dried at 120°C.

(xi) Dichlorobis(N-carboethoxy-4-toluenethioamidato)platinum(IV)

To a mixture of H_2PtCl_6 (0.41 g, 1 mmol) in ethanol (25 ml) and ligand Hctt (0.45 g, 2 mmol) in ethanol (10 ml) was added 2 ml of dil. HCl (1:1), concentrated on a water bath (~7-8 ml). The light brown precipitate was obtained on addition of water, filtered, washed with hot water, dried at 120 C and recrystallized from ethanol/ether (1:2).

(xii) Reaction of $[RhCl(PPh_3)_3]$ with Hctt

A solution of $[RhCl(PPh_3)_3]$ (0.46 g, 0.5 mmol) in CH_2Cl_2 (25 ml) was added to a solution of Hctt (0.14 g, 0.66 mmol) in CH_2Cl_2 (25 ml). The reddish brown solution so obtained was refluxed on a water bath for 15 min, and evaporated to dryness. The oily mass thus obtained was dissolved in CH_2Cl_2(5 ml) and filtered. Petroleum ether (40-60°C) (20 ml) was added to initiate precipitation and cooled to 0°C. The yellow complex thus precipitated was separated by centrifugation, washed with petroleum ether and dried *in vacuo*.

(xiii) Reaction of $[Pd(PPh_3)_4]$ with Hctt

Freshly prepared $[Pd(PPh_3)_4]$ (0.1 g, 0.1 mmol) in CH_2Cl_2 (30 ml) was added to a stirring solution of Hctt (0.07 g, ca. 0.3 mmol) in CH_2Cl_2 (10 ml). The reaction mixture was refluxed for 1-2 hrs under dry N_2 atmosphere. The colour of the solution changed from yellow to dark brown, concentrated to ca. half volume under reduced pressure, added petroleum ether (50 ml) (40-60°C) to give yellow compound, separated by centrifugation, washed with petroleum ether, and dried *in vacuo*.

(xiv) Reaction of $[Pt(PPh_3)_4]$ with Hctt

Freshly prepared $[Pt(PPh_3)_4]$ (0.12 g, 0.1 mmol) in CH_2Cl_2 (30 ml) was added to a stirring solution of Hctt (0.7 g, ca. 0.3 mmol) in CH_2Cl_2 (10 ml). The reaction mixture was refluxed for 4-5 hrs under dry N_2 atmosphere, concentrated to ca. half volume under reduced pressure, added petroleum ether (60-80°) to give orange compound, separated by centrifugation, washed with petroleum ether and dried in vacuo.

II.1.2 Sulfur Abstraction from Hctt by Soft Metal Ions

A water solution of metal salts* (~1 mmol) (25 ml) was mixed with ethanolic solution of Hctt (~1.5 mmol) (25 ml). The reaction mixture was refluxed for 2-4 hrs. The respective sulfides of Ag_2S (black), CuS (black), PbS (black), Hg_2S (black) and CdS

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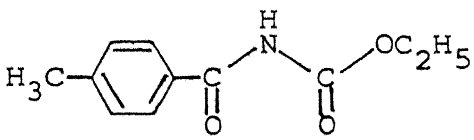
*$AgNO_3$, $CuCl_2$, $Pb(NO_3)_2$, $HgCl_2$ and $CdSO_4$.

(yellow) were precipitated and characterized after separation. In case of $AgNO_3$, yellow suspension is obtained which turns black (Ag_2S) on refluxing whereas in case of $HgCl_2$ a white compound was obtained which on refluxing gives black Hg_2S. In case of Hg^{++}, its reduction to Hg^+ takes place along with abstraction of sulfur of the ligand by the metal ion. The filtrate obtained from reaction of $AgNO_3$ and Hctt was evaporated to dryness on steam-bath, and the residue was crystallized from chloroform. These crystals were recrystallized from the mixture of carbon tetrachloride and ethyl acetate (1:1). The resulting needle shaped colourless crystalline compound was characterized as:



Abstraction of sulfur by soft metal ions from similar ligand was also reported earlier from our laboratory.

II.1.3 Analyses

Estimation of Copper, Cobalt, Nickel, Palladium and Platinum[1]

A weighed amount of the complex was decomposed by digesting it with aqua regia for some time until the resulting residue gave a transparent solution when taken in dil. mineral acids. It was was filtered and filtrate was made neutral if necessary by repeated evaporation with water and the residue was dissolved in water. Copper was estimated as $[Cu(en)_2][HgI_4]$, cobalt as $Co(C_5H_5N)_4(SCN)_2$ (precipitation with pyridine and ammonium thiocyanate); nickel as $Ni(C_4H_7O_2N_2)_2$ (precipitation with dimethyl

glyoxime).

For the estimations of palladium and platinum, samples were decomposed in aqua-regia. The excess nitric acid was removed by repeated evaporation with HCl. The residue was taken in dil. HCl (10^{-3} M) and palladium was estimated as $Pd(C_4H_7O_2N_2)_2$ and platinum as $[(NH_4)_2PtCl_6]$ in the solution.

Estimation of Phosphorus[2]

Samples were decomposed with a fusion mixture of (Na_2O_2: sugar:$NaNO_3$ :: 20:1:3 in a parr-bomb). The melt was extracted with water and heated to SO_3 fumes after adding concentrated H_2SO_4. It was diluted with water and filtered if necessary. In the filtrate phosphorus was estimated as ammonium phosphomolybdate.

Estimation of Halide and Sulfur

For the estimations of halide and sulfur, the complexes were decomposed by fusing a weighed amount of complex with $NaNO_3$ and NaOH (8 and 64 times of the sample, respectively) in a nickel crucible for $\sim$ 10 minutes. After cooling the crucible and extracting the residue with water, the solution was filtered, neutralised with dil. HNO_3 (in case of halide) or dil. HCl (in case of sulfate. Halides were estimated as AgCl and sulfur as $BaSO_4$ in the resulting solution.

The analytical data are presented in Table II.1.

II.2 RESULTS AND DISCUSSION

II.2.1 Reactions

The complexation reactions of metal salts with the ligand (Hctt) can be described by the following equations:

$$\text{Metal chloride} + 2\ Hctt \longrightarrow M(II)(ctt)_2 + 2\ HCl \qquad ..\ (1)$$

(metal chloride = $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $PdCl_2.2H_2O$, K_2PtCl_4).

$$MCl_2 + 2\ Hctt + Py \longrightarrow M(ctt)_2Py + 2\ HCl \qquad ..\ (2)$$

(M = Ni, Co)

$$RuCl_3.3H_2O + 3\ Hctt \longrightarrow Ru(ctt)_3 + 3\ HCl + 3\ H_2O \qquad ..\ (3)$$

$$2\ RuCl_3.3H_2O + 4\ Hctt \xrightarrow{Zn/THF} 2\ Ru(ctt)_2 + 4\ HCl + 6H_2O \qquad ..\ (4)$$

$$RhCl_3.3H_2O + 2\ Hctt \longrightarrow Rh(ctt)(Hctt)Cl_2 + HCl + 3H_2O \qquad ..\ (5)$$

$$H_2PtCl_6 + 2\ Hctt \longrightarrow Pt(ctt)_2Cl_2 + 4\ HCl \qquad ..\ (6)$$

The ligand functions as a reducing as well as a coordinating agent when it reacts with hexaamine cobalt(III) chloride.

Part of the ligand gets bound to reduced metal ion, i.e., Co(II) and the remaining Hctt is oxidized to give a dimer with sulfur-sulfur bond. The dimer has been isolated and characterized. The dimer does not ligate.

The following steps describe the details of the chemical reaction:

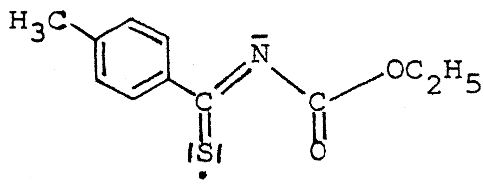
$$[Co(NH_3)_6]Cl_3 + e \longrightarrow [Co(H_2O)_6]Cl_2 + 6\ NH_3 + Cl^- + 6\ H_2O \quad .. \text{(i)}$$

$$Hctt \longrightarrow ctt^{\bullet} + H^+ + e \quad .. \text{(ii)}$$

$$2\ ctt^{\bullet} \longrightarrow (ctt)_2 \quad .. \text{(iii)}$$

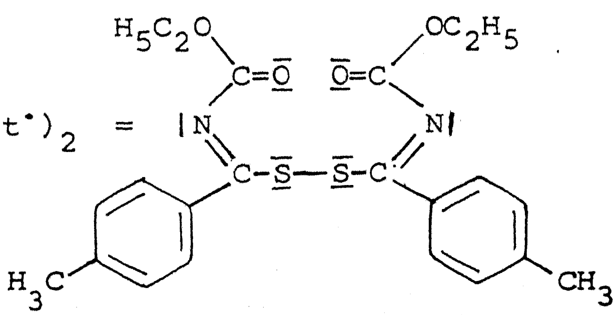
$$[Co(H_2O)_6]Cl_2 + 2\ Hctt \longrightarrow Co(ctt)_2 + 6\ H_2O + 2\ HCl \quad .. \text{(iv)}$$

$ctt^{\bullet}$ =



Radical

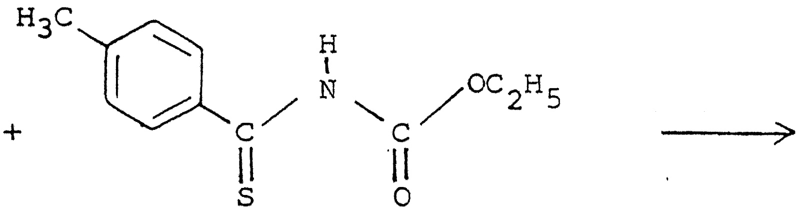
$(ctt^{\bullet})_2$ =



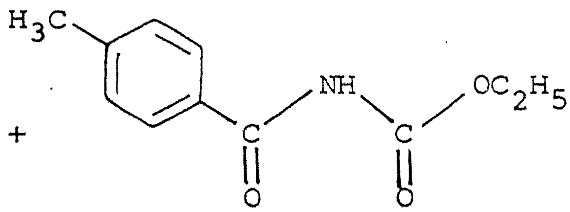
Dimer

With soft metal ions, on refluxing, instead of complexation, sulfur abstraction takes place, resulting in the formation of metal sulfide and oxygenated form of the ligand according to the following equation:

Metal salt +

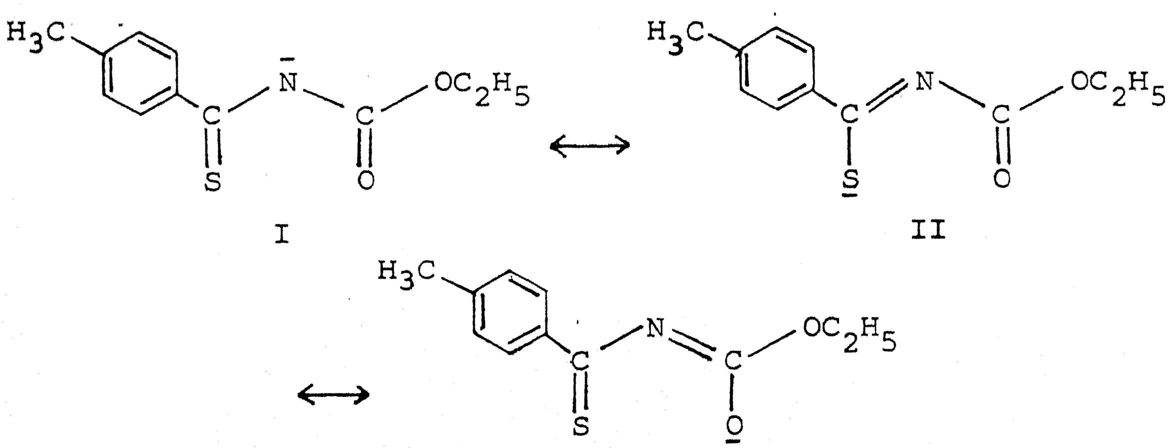


Metal sulfide +



II.2.2 IR Spectra

The donor ability of the ligand and the shifts of various i.r. bands in the spectra of the complexes can be best understood in terms of the resonance structures of the anion given below:



I II III

The position of the major bands of interest are shifted in the spectra of complexes. The changes in i.r. spectra and the inferences drawn regarding the site of bonding are summarised below:

A band at 3220 cm^{-1} in the spectrum of the ligand due to ν(NH) disappeared in the spectra of the complexes. This could probably be due to one replaceable hydrogen of NH group, the metal can form either a simple salt by linking with one nitrogen or an inner complex by forming a bond with nitrogen and thiocarbonyl sulfur or carbonyl oxygen. Two bands at 690 and 620 assigned to τ(NH) disappeared in the spectra of the complexes, confirming deprotonation of the ligand.

The range for C-N stretching in the ligand and its complexes lies between the ν(C=N) and ν(C-N) stretching frequencies in the 1640-1690 and 1250-1350 cm^{-1} range, respectively. Based on this observation the band at 1585 cm^{-1} in the ligand is assigned to ν(C$\cdots$N) (bond having double bond character).[3] The band at 1585 cm^{-1} ν(C$\cdots$N) in the ligand shifts to lower frequencies on complexation. The lower frequency of the ν(C$\cdots$N) absorption is to be expected if nitrogen coordination is involved (structure I).[4]

A band at 1540 cm^{-1} in the ligand is assigned to the thioamide band I [δ(N-H) + ν(C-N)] which disappears in the spectra of the complexes, indicating that mixing of δ(N-H) and ν(C-N) may be absent when the hydrogen of the N-H group is replaced by metal ion.

For Ni(II), Pd(II), Ru(II) and Ru(III) complexes structure I and III seem to predominate and the band at 1765 cm^{-1} assigned to ν(C=O) shifts towards lower wave numbers (ca. 115 cm^{-1}). A band at 1130 cm^{-1} assigned to ν(C=S), either remains stationary or goes up and thioamide band IV having major contribution of ν(C=S) (850 cm^{-1}) shifts to higher wave numbers (ca. 20 cm^{-1}). The above observations are indicative of non-involvement of thiocarbonyl sulfur in coordination and appreciably strong interaction of the metal ion with the carbonyl oxygen.

For the Cu(II), Co(II), Pt(II), Pt(IV), Rh(III) complexes forms I and II of the ligand appear to be operative. The thioamide band IV having a major contribution from ν(C=S) (850 cm^{-1}) shifts to lower wave numbers in the complexes (ca. 20 cm^{-1}) indicating the participation of thiocarbonyl sulfur in bond formation. The band due to ν(C=S) at 1130 cm^{-1} also goes to lower wave number. This further confirms the bonding through sulfur. The band at 1765 cm^{-1} ν(C=O) shifts to higher wave number or remains stationary. This indicates non-involvement of carbonyl oxygen in the coordination.

The band at 1360 cm^{-1}, assigned to the thioamide band II (δ_{N-H} + $\nu_{C\cdots N}$ + δ_{C-H}), undergoes unsystematic shits on complexation. No useful inferences could be drawn by making use of this band.

The band at 1075 cm^{-1} in the spectra of the ligand has been assigned to the thioamide band III (mainly due to ($\nu_{C\cdots N}$ + $\nu_{C\cdots S}$)

This band shows, as expected, a red shift on complexation in all the cases.

In the i.r. spectra of $Ni(ctt)_2py$ and $Co(ctt)_2py$, there seems to be extensive mixing between the bands of the ligand and those of pyridine, hence, characteristic bands of pyridine did not occur at its standard position. However, coordination of pyridine is almost certain as some of the bands characteristic of pyridine can be identified with small shifts. The bands at 604 cm^{-1} (in plane ring deformation) and 405 cm^{-1} (out-of-plane ring deformation) are shifted to higher frequencies 680 and 480 cm^{-1}, respectively in the spectra of the above two complexes.[5-7]

The appearance of new medium bands in the region 500-300 cm^{-1} is strong evidence of coordination by both nitrogen and oxygen or sulfur.

II.2.3 Magnetic Moment

All complexes except $Ni(ctt)_2py$, $Cu(ctt)_2$, $Co(ctt)_2$, $Co(ctt)_2$-py and $Ru(ctt)_3$ were found to be diamagnetic. The magnetic moment of $Co(ctt)_2py$ (2.05 BM) corresponds to one unpaired electron indicating a low spin square pyramidal structure. $Co(ctt)_2$ is paramagnetic having a magnetic moment of 2.1 BM indicating the square planar geometry of the complex. $Cu(ctt)_2$ is paramagnetic (1.99 BM) corresponding to one unpaired electron indicating a square planar or distorted octahedral geometry around the metal ion. The $Ru(ctt)_3$ complex is paramagnetic (1.73 BM) corresponding to one

unpaired electron. This indicates the distorted octahedral geometry of the complex. The diamagnetism of the $Ni(ctt)_2$ complex indicates strongly that it should be square planar, since another preferred orientation should show paramagnetism corresponding to two unpaired electrons.

II.2.4 Electronic Spectra

The electronic spectrum of the ligand (Hctt) in ethanol exhibited three strong bands at 450 nm, 310 nm and 270 nm, the first two bands may be assigned to intraligand transition (IL) $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, respectively, usually, the $n \rightarrow \pi^*$ transition involving N and S occur at lower energy and are less intense than the $\pi \rightarrow \pi^*$ transition. The band at 270 nm of the ligand may be due to intraligand charge transfer (CT).[8,9]

The electronic spectra of the complexes were also taken in ethanol. Most of the spectra showed almost continuous absorption in the visible region, therefore, some of the d-d transition expected for the respective complexes did not appear. The observed bands and their assignment are given in Table II.3. The Ni(II), Cu(II), Ru(II), Rh(III), Pd(II) and Pt(IV) complexes showed only intraligand transition with a small shift of +10 nm and therefore, were assigned accordingly. Both cobalt complexes showed a broad band at 475 nm, along with some intraligand transitions, which may be assigned to $d_{xz} \pm d_{yz} \rightarrow d_{x^2-y^2}$ transition.[10-13] The spectrum of the compound $Pt(ctt)_2$ showed a band at 415 nm which is probably

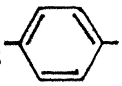
due to the d-d transition, $d_{x^2-y^2} \rightarrow d_{xy}$ $(^1A_{1g} \rightarrow {}^1B_{1g})$.[14]

All the bands of Hctt ligand were present with little shift in $[RhCl(Hctt)_2(PPh_3)]$, $[Pd(Hctt)_2(PPh_3)_2)$ and $[Pt(Hctt)_2(PPh_3)_2]$. A band at 450 nm in $[Pt(Hctt)_2(PPh_3)_2]$ is tentatively assigned to a M $\rightarrow$ L charge-transfer. The transition below 300 nm may be assigned to intraligand $\pi \rightarrow \pi^*$ transitions and their high intensity suggests that they are charge transfer or intraligand and not d-d transitions.

The i.r. evidence clearly indicates that the ligand acts as an NO/NS donor in these complexes, square planar geometry is assigned to Ni(II), Pd(II), Pt(II), Co(II) and Cu(II) complexes. Ru(III), Ru(II), Rh(III), Pt(IV) complexes are octahedrally coordinated, whereas $Ni(ctt)_2py$ and $Co(ctt)_2py$ are square pyramidal. In case the ligand functions as bidentate to one metal ion, it will result in four membered chelate ring (structure a) and this will result in stra specially in a case when the ligand acts as NO donor. In view of the above facts and the insolubility of the complexes in most of the non-coordinating organic solvents the complexes may have open polymeric structures with the nitrogen and oxygen atom of one ligand being bound to two different metal atoms (structure b). It is known that OS donor monothio-β-diketonates form exclusively cis-complexes with square planar coordinated metal ions and facial complexes with octahedrally coordinated metal ions.[15,16] Consequently, it is suggested that the Pt(II), Co(II), Cu(II) complexes (in which the ligand is NS)donor have the cis-square planar configuration). Although these structures contain a four membered ring,

they do not involve undue strain because of the large size of the sulfur atom. Four membered chelate rings are known with NS ligands.[17] Hence, inspite of the insolubility of the compounds, in case of the NS donor situation, both chelates and open polymeric structures (structures c and d) are equally probable.

<u>$RhCl(Hctt)_2(PPh_3)$</u>

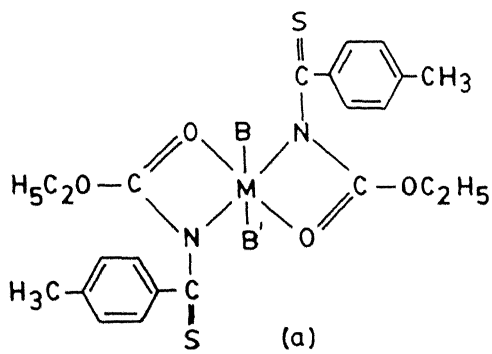
The thioamide band I ($\delta_{NH} + \nu_{CN}$) (1540 cm^{-1}) goes up (<u>ca</u>. 40 cm^{-1}) and $\nu_{C=O}$ (1765 cm^{-1})[18] shifts to lower wave numbers (<u>ca</u>. 35 cm^{-1}). $\nu_{C=S}$ (1130 cm^{-1}) remains unchanged after complexation. The shifts indicate the involvement of carbonyl oxygen in bond formation. The complex may be assigned to possess a square planar (trans) geometry. Band at 370 cm^{-1} and 330 cm^{-1} are due to $\nu(Rh\text{-}O)$[19] and $\nu(Rh\text{-}Cl)$, respectively.[20] Field desorption spectrum (FD/MS) of this complex was done in solution which shows the peaks at m/e of 884 [$RhCl(ctt)_2(PPh_3)$], 262 [(PPh_3)], 223 [(Hctt)], 117 [(CH_3--C≡N)].

<u>$Pd(Hctt)_2(PPh_3)_2$</u>

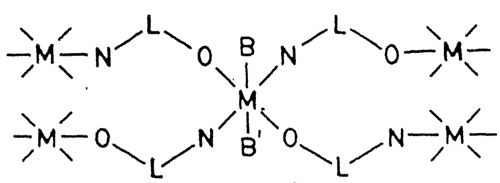
There is a band around 3300 cm^{-1} due to ν_{NH} in this complex, $\nu_{C=O}$ shifts to higher wave number (<u>ca</u>. 15 cm^{-1}), thioamide band IV and $\nu_{C=S}$ go down by 20 cm^{-1} and 10 cm^{-1}, respectively. Above shifts in the i.r. bands indicate the bonding through sulfur. Tetrahedral geometry is assigned for the complex.

<u>$Pt(Hctt)_2(PPh_3)_2$</u>

The band due to ν_{NH} (3220 cm^{-1}) could not be detected in the i.r. spectrum of this complex. The band due to $\nu_{C=O}$ (1765 cm^{-1}) goes up by <u>ca</u>. 35 cm^{-1}. Thioamide band IV and $\nu_{C=S}$ go down by 30 cm^{-1} and 10 cm^{-1}, respectively. These observations are indicative of bonding through thiocarbonyl sulfur. Tetrahedral geometry is proposed for the complex.

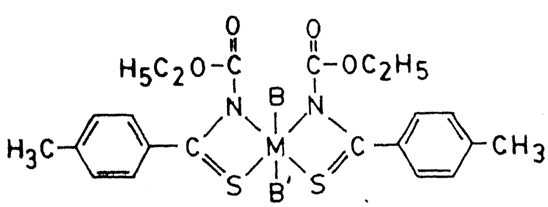


(a)

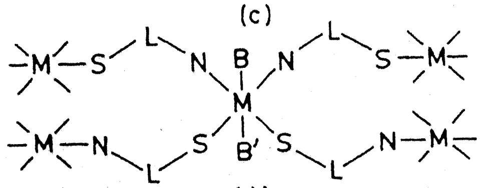


(b)

M = Ni (II) and Pd (II), B, B′ = Nil
M = Ni (II); B = Py, B′ = Nil



(c)



(d)

M = Co (II), Cu (II) and Pt (II); B, B′ = Nil
M = Rh (III) and Pt (IV); B, B′ = Cl

Table II.1 Analytical and Magnetic Data

Compound	Colour	M.P.‡ (°C)	Yield (%)	Analysis: Found (Calcd.) % C	H	N	M	S	Halide	μ_{eff} (B.M.)
1	2	3	4	5	6	7	8	9	10	11
[Ni(ctt)$_2$]	Brown	159-60	50	52.4 (52.3)	4.7 (4.8)	5.4 (5.5)	11.6 (11.7)	12.8 (12.7)	-	DM
[Ni(ctt)$_2$PY]	Dark Brown	145-47	52	55.6 (55.8)	5.2 (5.0)	7.4 (7.2)	10.2 (10.0)	11.4 (11.0)	-	3.14
[Co(ctt)$_2$]	Black Brown	>240	50	52.4 (52.3)	4.6 (4.8)	5.3 (5.5)	11.5 (11.7)	12.6 (12.7)	-	2.10
[Co(ctt)$_2$PY]	Dark Greenish	82-83	54	55.5 (55.8)	5.3 (5.0)	7.5 (7.2)	10.3 (10.0)	11.3 (11.0)	-	2.05
[Cu(ctt)$_2$]	Brown	175d	55	52.4 (52.0)	4.5 (4.7)	5.3 (5.5)	12.7 (12.5)	12.8 (12.6)	-	1.99
[Ru(ctt)$_3$]	Black	>240	53	51.8 (51.6)	4.3 (4.7)	5.6 (5.5)	-	12.8 (12.5)	-	1.73
[Ru(ctt)$_2$]	Reddish Brown	170	48	48.5 (48.2)	4.5 (4.4)	5.4 (5.1)	-	11.9 (11.7)	-	DM
[Rh(ctt)(Hctt)Cl$_2$]	"	>240	60	42.8 (42.6)	4.3 (4.0)	4.8 (4.5)	-	10.6 (10.3)	11.8 (11.5)	DM

...contd

Table II.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11
$[RhCl(Hctt)_2(PPh_3)]$	Yellow	120- 2	60	56.3 (56.9)	4.6 (4.9)	3.1 (3.3)	-	7.4 (7.6)	4.4 (4.2)	DM
$[Pd(ctt)_2]$	Yellow-ish Brown	150-52	72	48.2 (48.0)	4.5 (4.3)	5.5 (5.1)	19.5 (19.3)	11.5 (11.7)	-	DM
$[Pd(Hctt)_2(PPh_3)_2]$	Yellow	195d	52	64.4 (64.7)	5.0 (5.2)	2.4 (2.6)	9.8 (9.9)	5.7 (5.9)	-	DM
$[Pt(ctt)_2Cl_2]$	Brown	>240	58	37.4 (37.1)	3.6 (3.4)	3.6 (3.9)	27.5 (27.4)	8.8 (9.0)	9.6 (9.9)	DM
$[Pt(ctt)_2]$	Brown	>240	65	41.5 (41.3)	3.5 (3.8)	4.8 (4.4)	30.7 (30.5)	10.4 (10.0)	-	DM
$[Pt(ctt)_2(PPh_3)_2]$	Orange	193-95	55	59.4 (59.7)	4.6 (4.8)	2.2 (2.4)	- (16.7)	5.3 (5.5)	-	DM

* At 293 K and uncorrected for diamagnetism; DM = diamagnetic; d = decomposes.

‡ Melting points are uncorrected.

Table II.2 Major i.r. Bands Comparison of i.r. Spectra of Complexes with Ligand (cm^{-1})

Compound	ν(NH)	ν(C$\cdots$N)	ν(C=O)	ν(C=S)	Thioamide bands				Possible Coordination
					I	II	III	IV	
[Hctt]	3220	1585m	1765s	1130s	1540s	1360s	1075s	850s	
[$Ni(ctt)_2$]	-	1500s	1650s	1150s	-	1370s	1070s	875s	N and O
[$Ni(ctt)_2py$]	-	1495s	1650s	1150s	-	1350m	1060s	880s	N and O
[$Co(ctt)_2$]	-	1580s	1800s	1120s	-	1360s	1070m	825s	N and S
[$Co(ctt)_2py$]	-	1520s	1800s	1120s	-	1370s	1050s	825s	N and S
[$Cu(ctt)_2$]	-	1520s	1765s	1120s	-	1370s	1050s	820s	N and S
[$Ru(ctt)_3$]	-	1500br,s	1740s	1130s	-	1380m	1040s	850s	N and O
[$Ru(ctt)_2$]	-	1500br,s	1730s	1130s	-	1370m	1040s	870m	N and O
[$Rh(ctt)(Hctt)Cl_2$]	-	1500s	1770s	1100m	-	1380m	1040m	825s	N and S
[$RhCl(Hctt)_2(PPh_3)_2$]	-	-	1730s	1140m	1580s	1370s	1070s	870s	O
[$Pd(ctt)_2$]	-	1500s	1740s	1140m	-	1370s	1040s	875s	N and O
[$Pd(Hctt)_2(PPh_3)_2$]	3300	-	1780s	1120s	1550s	1370s	1075s	830s	S
[$Pt(ctt)_2Cl_2$]	-	1480s	1780s	1120m	-	1420m	1050s	830s	N and S
[$Pt(ctt)_2$]	-	1500s	1770s	1120w	-	1410m	1050s	830s	N and S
[$Pt(Hctt)_2(PPh_3)_2$]	-	-	1800s	1120s	1560s	1375s	1070s	820s	S

Table II.3 Electronic Spectra of Ligand and Complexes

Compounds	Band position λ_{max} (nm)	Assignments
1	2	3
Ligand [Hctt]	450	$n \rightarrow \pi^*$
	310	$\pi \rightarrow \pi^*$
	270	ILCT
$[Ni(ctt)_2]$	305(br)	IL
	260(br)	CT
$[Ni(ctt)_2py]$	300(br)	IL
	260	CT
$[Co(ctt)_2]$	475(br)	$d_{xz} \pm d_{yz} \rightarrow d_{x^2-y^2}$
	305	IL
	235(br)	CT
$[Co(ctt)_2py]$	475(br)	$d_{xz} \pm d_{yz} \rightarrow d_{x^2-y^2}$
	300	IL
	260	CT
	230	CT
$[Cu(ctt)_2]$	265	CT
	260	CT
	250	CT
	245	CT
$[Ru(ctt)_3]$	310	IL
	260	CT
	255	CT
$[Ru(ctt)_2]$	310	IL
	260	CT
	255	CT
$[Rh(ctt)(Hctt)Cl_2]$	320	IL
	310	IL
	240	CT

...contd.

Table II.3 (contd.)

1	2	3
$[RhCl(Hctt)_2(PPh_3)]$	310	IL
	230(sh)	CT
$[Pd(ctt)_2]$	310	IL
	265	CT
$[Pd(Hctt)_2(PPh_3)_2]$	280	IL
	235	CT
$[Pt(ctt)_2Cl_2]$	310	IL
	260	CT
	250	CT
$[Pt(ctt)_2]$	415	$^1A_{1g} \rightarrow {}^1B_{1g}$
	350	IL
	320	CT
$[Pt(Hctt)_2(PPh_3)_2]$	285	IL
	230	CT

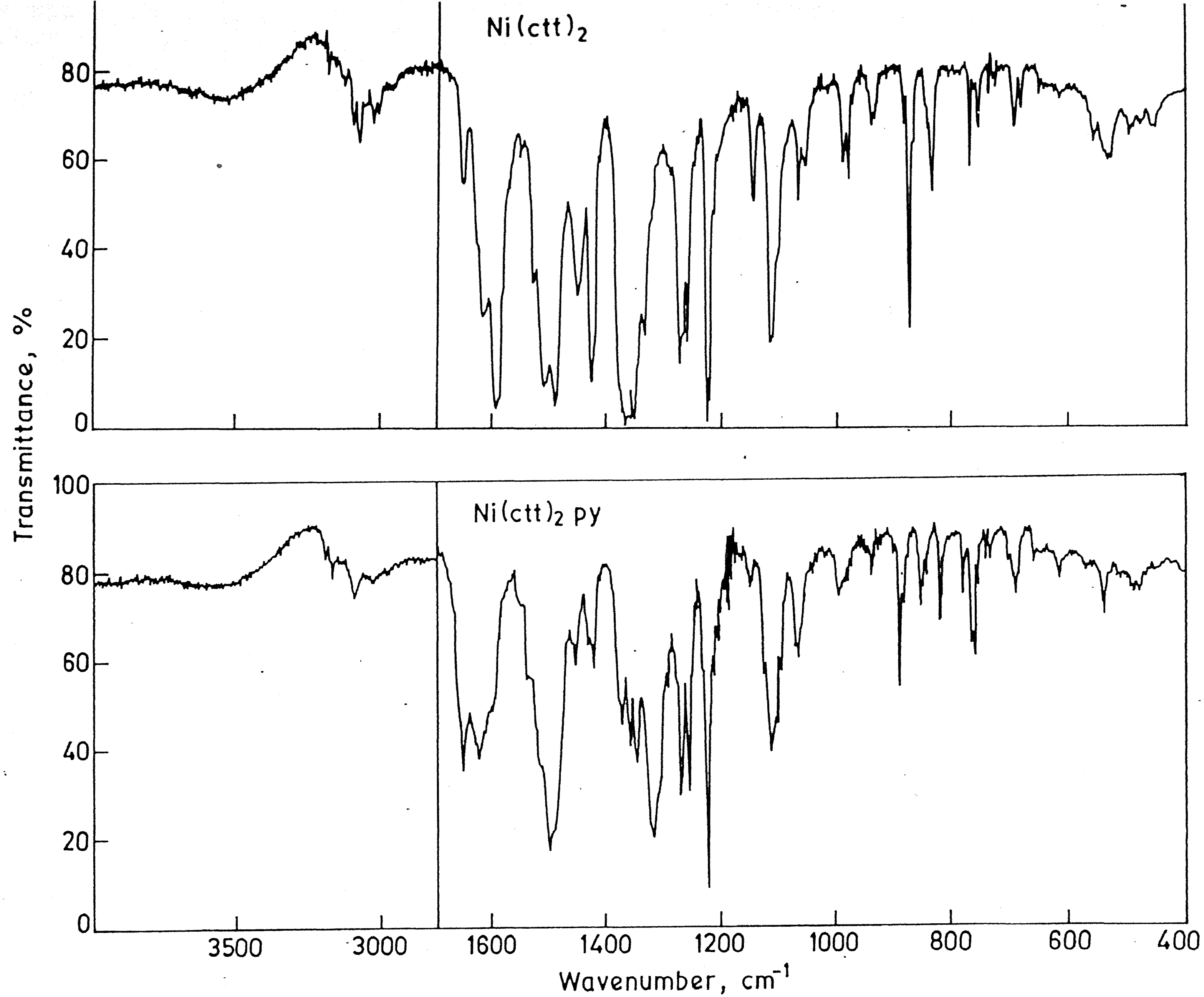

Ni(ctt)$_2$
Ni(ctt)$_2$ py
Transmittance, %
100
80
60
40
20
0
3500
3000
1600
1400
1200
1000
800
600
400
Wavenumber, cm^{-1}

Fig. II.1

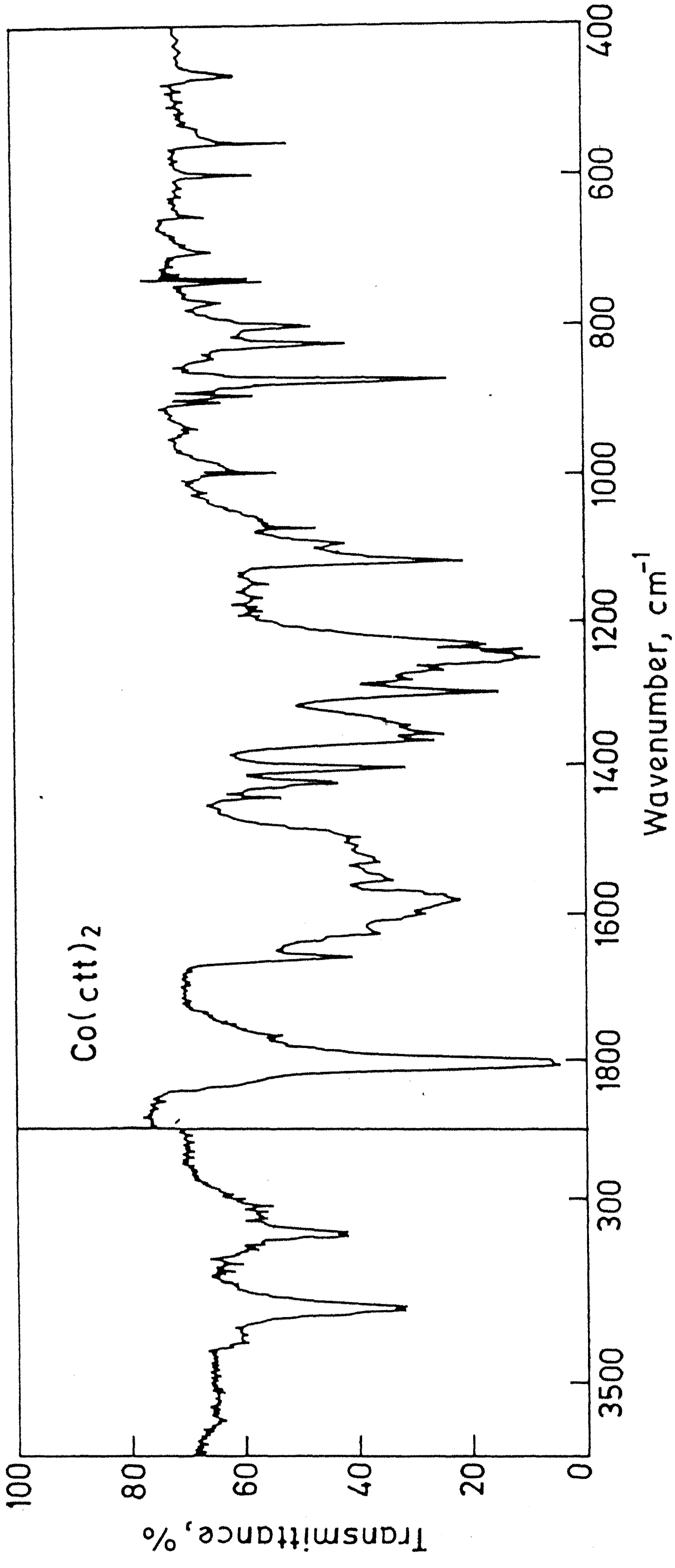

Co(ctt)$_2$
Transmittance, %
100
80
60
40
20
0
3500
300
1800
1600
1400
1200
1000
800
600
400
Wavenumber, cm^{-1}

Fig. II.2

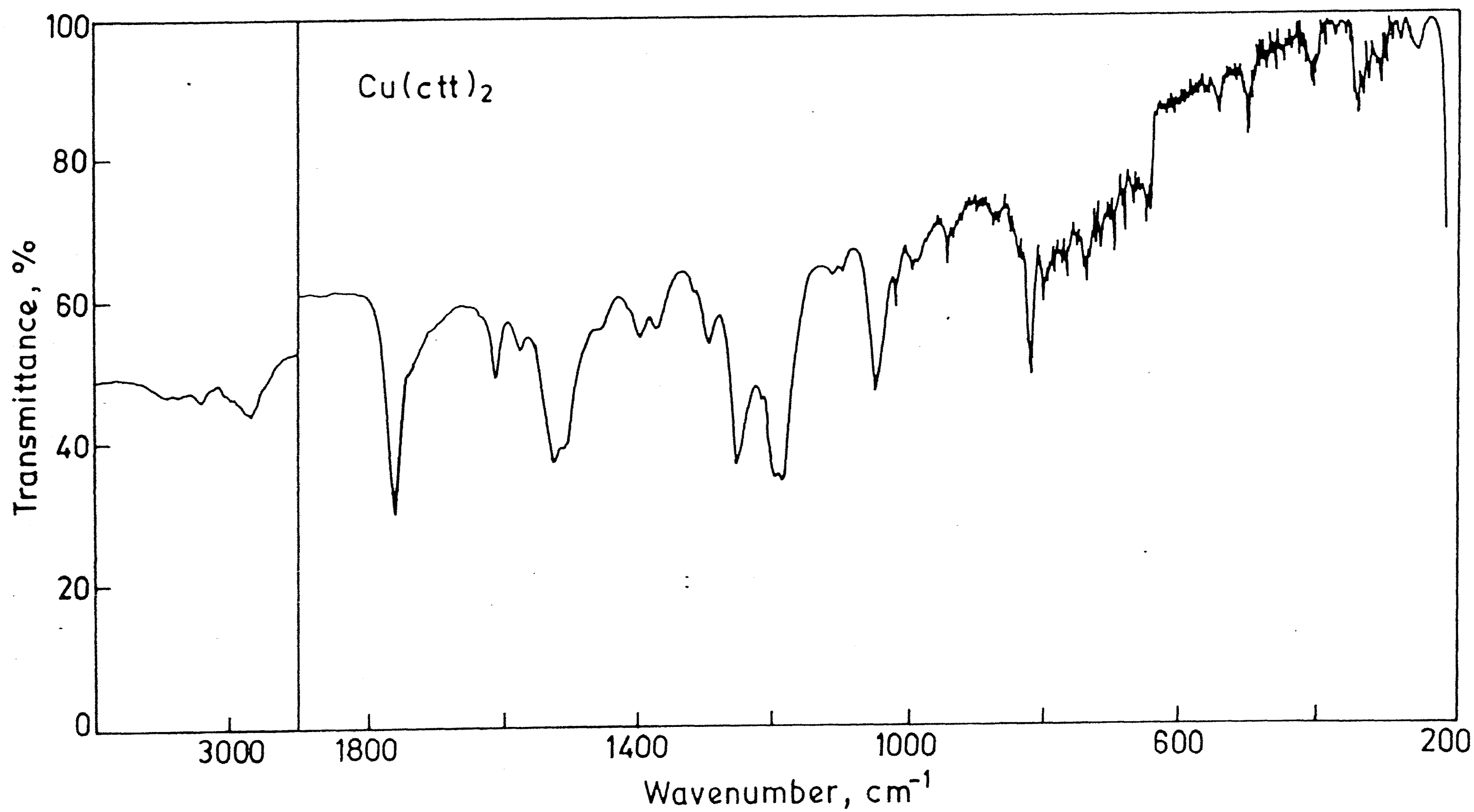
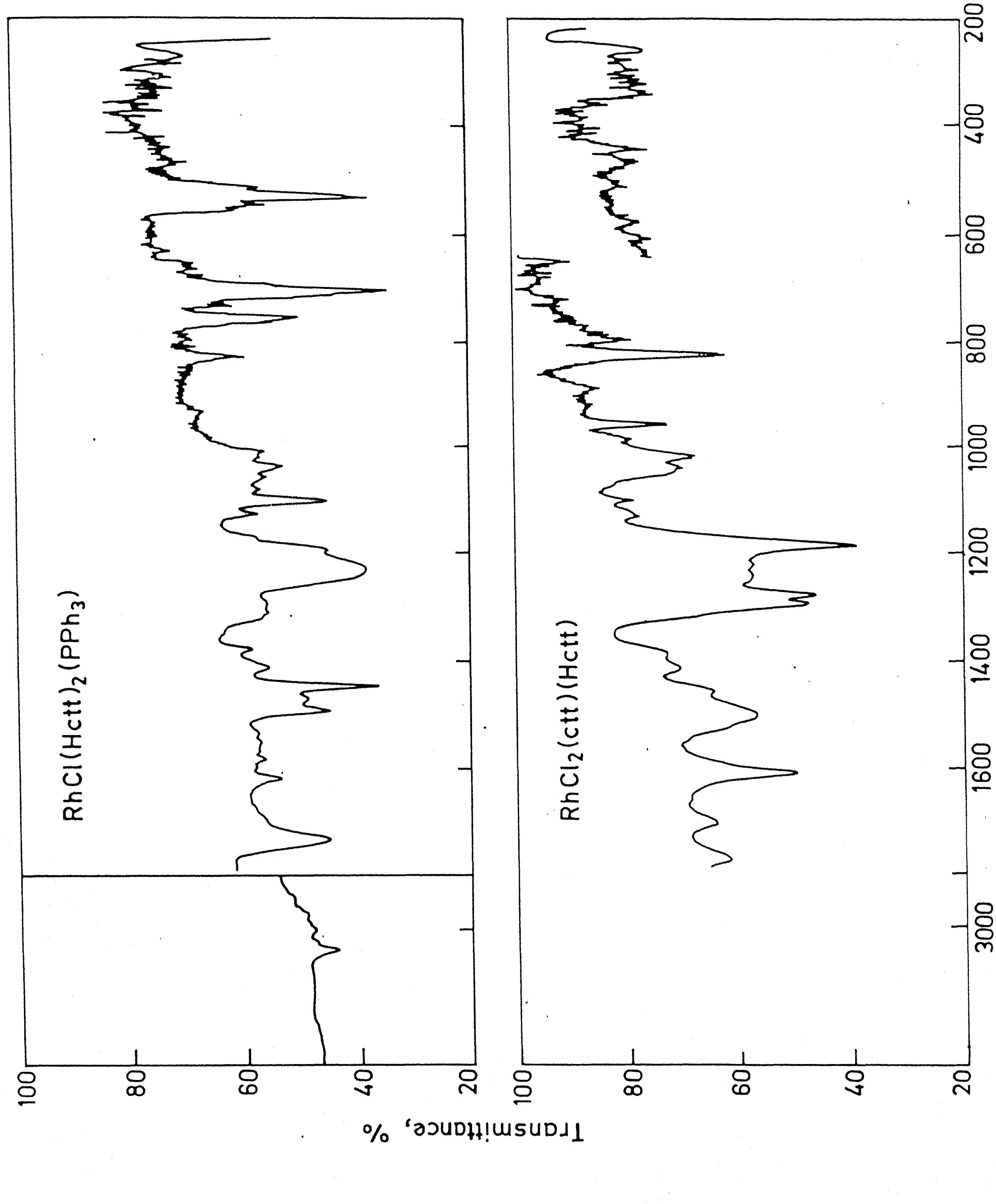

Cu(ctt)$_2$
Transmittance, %
0
20
40
60
80
100
3000
1800
1400
1000
600
200
Wavenumber, cm^{-1}

Fig. II.3


RhCl(Hctt)$_2$(PPh$_3$)
RhCl$_2$(ctt)(Hctt)
Transmittance, %
100
80
60
40
20
3000
1600
1400
1200
1000
800
600
400
200

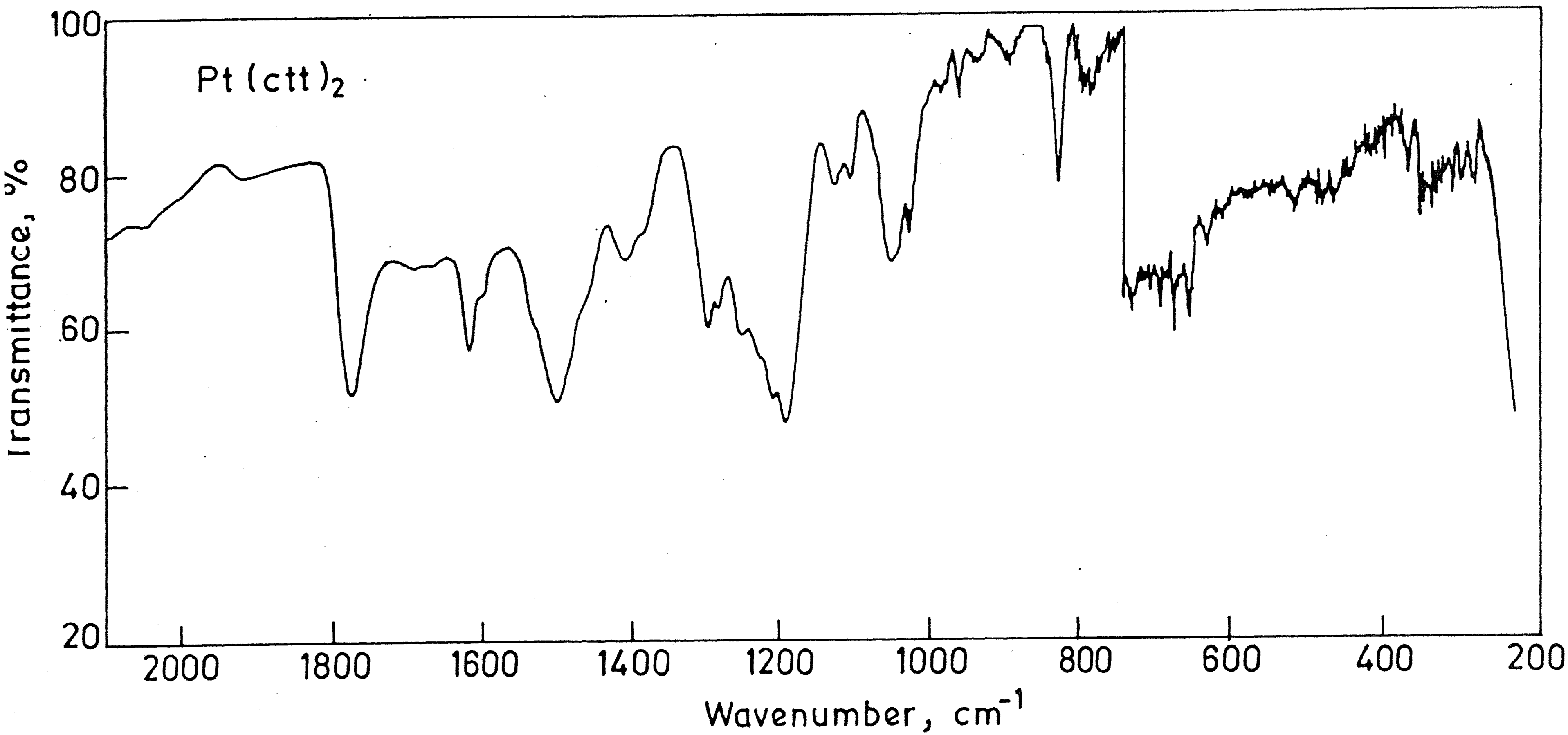

Pt (ctt)$_2$
Transmittance, %
100
80
60
40
20
2000
1800
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig. II.5

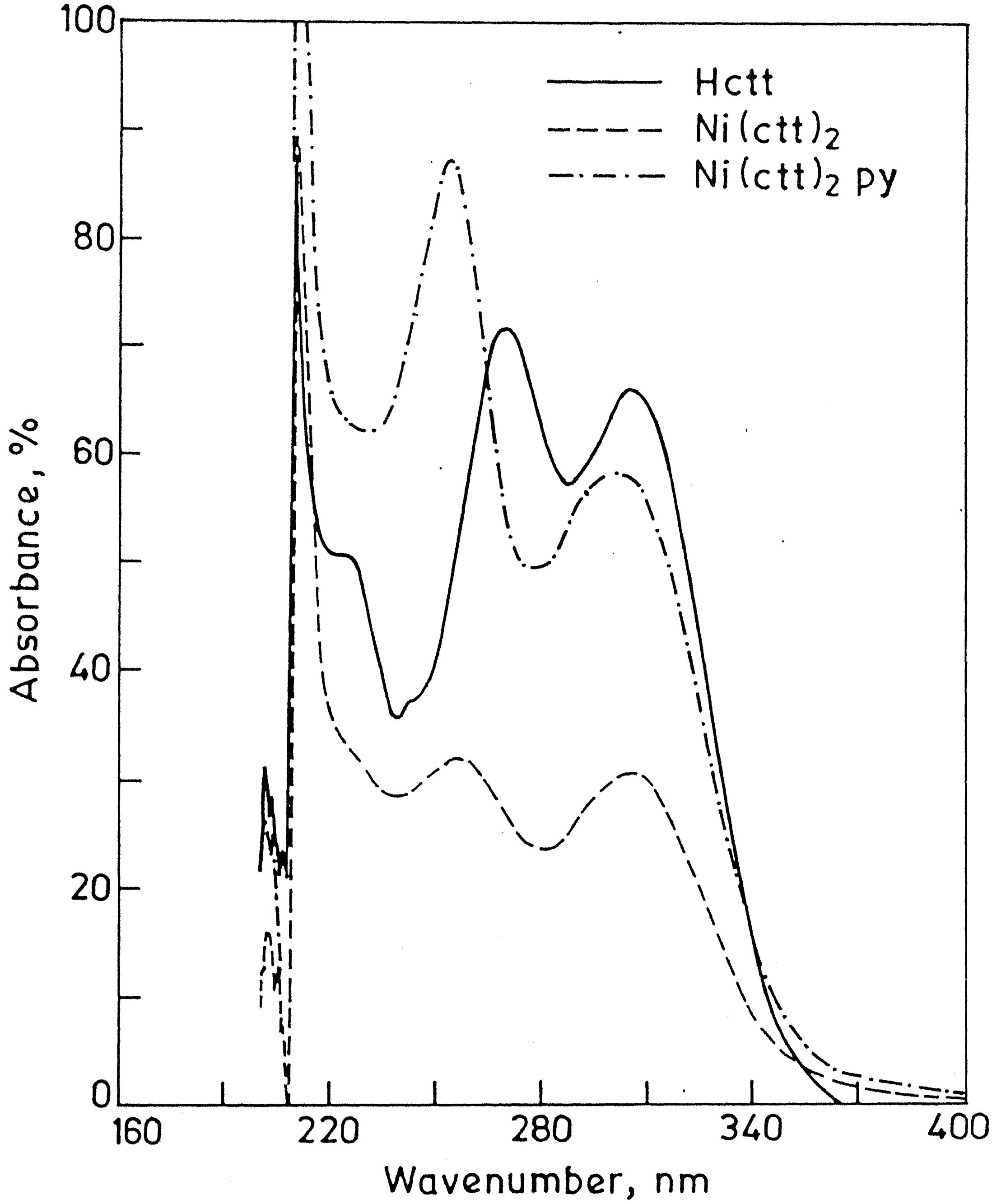
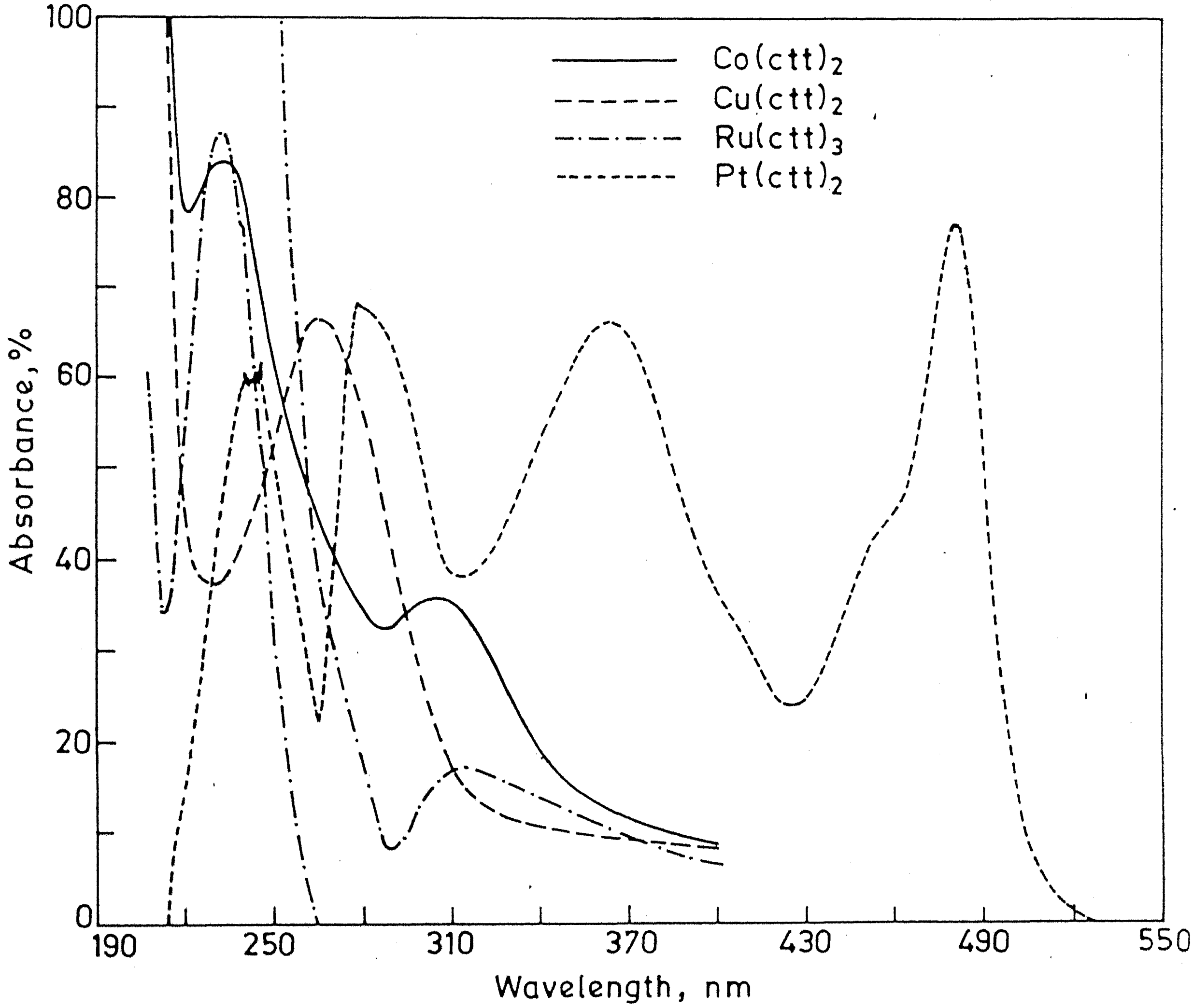
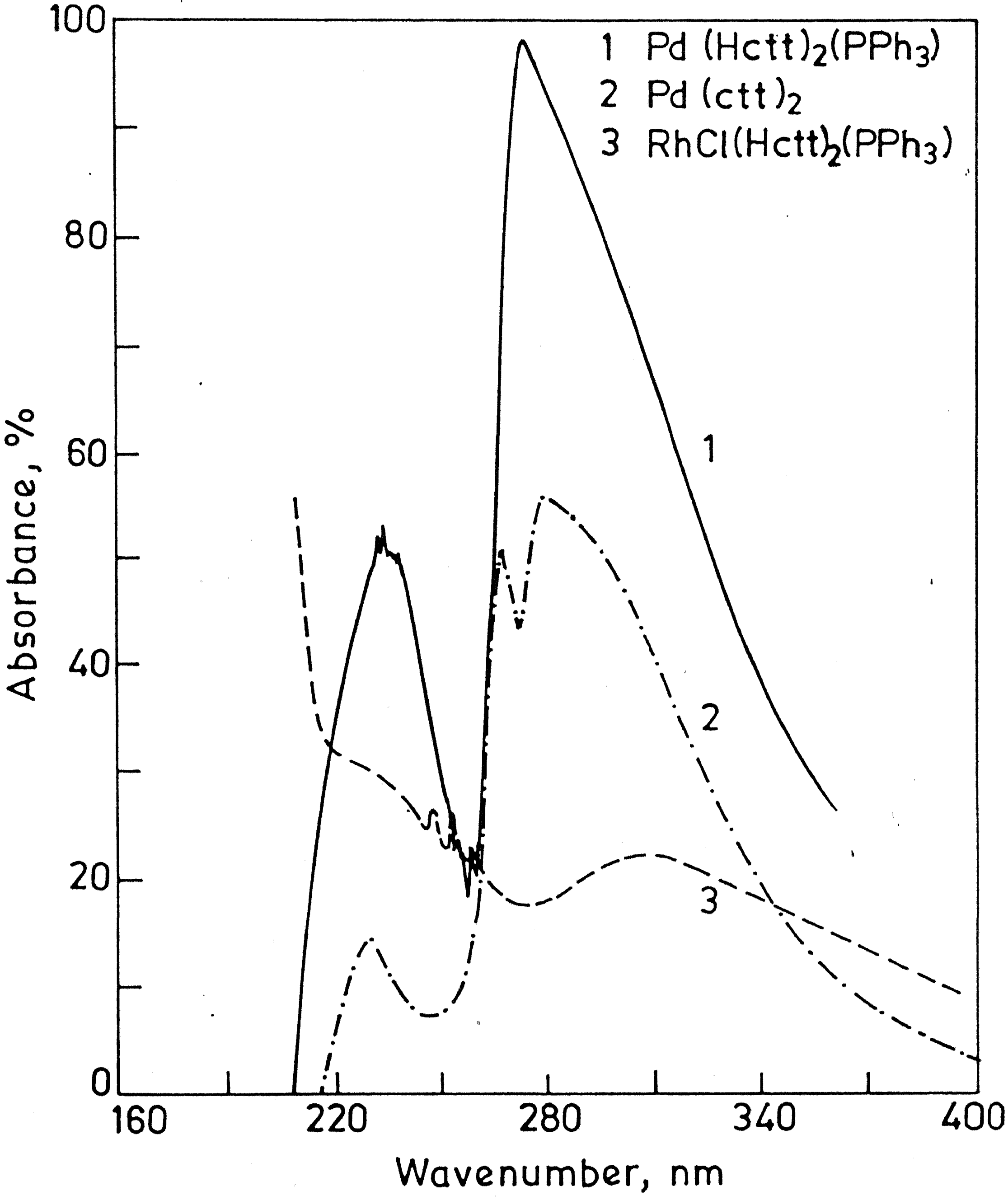

Hctt
Ni(ctt)2
Ni(ctt)2 py
Absorbance, %
0
20
40
60
80
100
160
220
280
340
400
Wavenumber, nm

Fig. II.6



100
80
60
40
20
0
Absorbance, %
190
250
310
370
430
490
550
Wavelength, nm
Co(ctt)$_2$
Cu(ctt)$_2$
Ru(ctt)$_3$
Pt(ctt)$_2$

Fig. II.7



1 Pd (Hctt)$_2$(PPh$_3$)
2 Pd (ctt)$_2$
3 RhCl(Hctt)$_2$(PPh$_3$)
100
80
60
40
20
0
Absorbance, %
1
2
3
160
220
280
340
400
Wavenumber, nm

Fig. II.8

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CHAPTER III

COORDINATION CHEMISTRY OF NEW SULFUR-CONTAINING LIGANDS: TRANSITION METAL COMPLEXES OF N-CARBOETHOXY-1-PYRROLE THIOAMIDE (A NEW THIOAMIDE LIGAND)*

In this chapter, reactions of N-carboethoxy-1-pyrrolethioamide (Hcpt) with a variety of transition metal ions leading to the formation of $[M^{II}(cpt)_2]$ (M = Ni, Cu, Pd, Pt), $[M^{II}(cpt)_2(py)]$ (M = Co, Ni), $[Rh^{I}Cl(Hcpt)(PPh_3)]_2$ and $[M^{III}Cl(cpt)_2(H_2O)]$ (M = Ru, Rh) are described. Reaction of Hcpt with Ag(I), Cu(II), Pb(II), Hg(II) and Cd(II) under refluxing conditions yields the correspond ing sulfides and an oxygenated form of the ligand (Hcpt), which wa characterized as  N-C(=O)-NH-C(=O)-OC_2H_5. All metal complexes have bee characterized on the basis of analytical, i.r., electronic spectra and magnetic measurement studies.

III.1 EXPERIMENTAL

All the chemicals used were either AR or chemically pure grade. The methods of analyses and the instruments used were same as described in earlier chapters. Ligand was prepared by the literature method (see appendix).

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*Bull. Chem. Soc. Japan, 59, 000 (1986).

III.1 Preparation of the Complexes

(i) Bis(N-carboethoxy-1-pyrrolethioamidato)copper(II)

A cold solution of Hcpt (0.80 g, 4 mmol) in ethanol (25 ml) was added dropwise to an ice-cold solution of $CuCl_2.2H_2O$ (0.34 g, 2 mmol) in water (25 ml). Immediate light brown precipitate results. The precipitate was centrifuged, washed with water, ethanol and ether, dried *in vacuo*.

(ii) Bis(N-carboethoxy-1-pyrrolethioamidato)(pyridine)nickel(II)

A cold solution of Hcpt (0.80 g, 4 mmol) in ethanol (10 ml) was added dropwise to an ice-cold solution of $NiCl_2.6H_2O$ (0.48 g, 2 mmol) in water (25 ml) containing 10 ml of pyridine which resulted in the precipitation of green compound. The compound was filtered, washed with water and dried *in vacuo*.

(iii) Bis(N-carboethoxy-1-pyrrolethioamidato)nickel(II)

This compound was obtained as yellow solid by heating bis-(N-carboethoxy-1-pyrrolethioamidato)pyridine-nickel(II) at 90-100^{o}C.

(iv) Bis(N-carboethoxy-1-pyrrolethioamidato)(pyridine)cobalt(II)

A cold solution of Hcpt (0.80 g, 4 mmol) in ethanol (10 ml) was added dropwise to an ice cold solution of $CoCl_2.6H_2O$ (0.48 g, 2 mmol) in water (25 ml) containing 10 ml of pyridine which resulted in the precipitation of brown compound. The compound was filtered, washed with water and dried *in vacuo*.

(v) (N-Carboethoxy-1-pyrrolethioamidato)silver(I)

A solution of Hcpt (0.40 g, 2 mmol) in ethanol (10 ml) was added to a stirred solution of $AgNO_3$ (0.34 g, 2 mmol) in water (10 ml) at room temperature. The resulted yellow precipitate was filtered off, washed with water, ethanol and ether and dried *in vacuo*. This compound decomposes on heating or on standing for mor than one day.

(vi) Aquachlorobis(N-carboethoxy-1-pyrrolethioamidato)ruthenium(II

$RuCl_3.3H_2O$ (0.26 g, 1 mmol) in H_2O (25 ml) was added to an ethanolic solution (25 ml) of Hcpt (0.40 g, 2 mmol). The reaction mixture was refluxed on water bath for 1-2 hr. The black-brown complex which precipitated out was separated by centrifugation, washed successively several times with water, ethanol and ether, dried *in vacuo*.

(vii) Aquachlorobis(N-carboethoxy-1-pyrrolethioamidato)rhodium(III

A solution of Hcpt (0.40 g, 2 mmol) in ethanol (10 ml) was added to stirred solution of $RuCl_3.3H_2O$ (0.26 g, 1 mmol) in H_2O (50 ml). The resulting orange colloidal solution was digested on water bath for 2 hrand the reddish orange rhodium complex was then filtered, washed with water, ethanol and ether and dried *in vacuo*.

(viii) Di-μ-chlorobis(N-carboethoxy-1-pyrrolethioamidato)bis(triphenylphosphine)dirhodium(I)

A solution of Hcpt (0.13 g, 0.6 mmol) in dichloromethane (25 was mixed with the solution of $[RhCl(PPh_3)_3]$ (0.46 g, 0.5 mmol) in dichloromethane (25 ml). The resulting mixture was refluxed for 1 min, cooled at room temperature, concentrated to 5 ml at reduced pressure and added petroleum ether. The yellow complex thus forme

was filtered, washed with petroleum ether and dried *in vacuo*.

(ix) Bis(N-carboethoxy-1-pyrrolethioamidato)palladium(II)

A solution of Hcpt (0.40 g, 2 mmol) in ethanol (20 ml) was added to hot solution of $PdCl_2.2H_2O$ (0.21 g, 1 mmol) in water (50 ml). Immediately yellow palladium complex appeared. The precipitate was filtered washed with water, ethanol and ether and dried *in vacuo*.

(x) Bis(N-carboethoxy-1-pyrrolethioamidato)platinum(II)

A solution of Hcpt (0.40 g, 2 mmol) in ethanol (25 ml) was added to solution of H_2PtCl_6 (0.41 g, 1 mmol) in water (25 ml). The mixture was refluxed for 1 hr. The dark brown precipitate thus appeared, was separated, washed with water, ethanol and ether and dried in air.

(xi) Sulfur abstraction from Hcpt by soft metal ions

An aqueous solution of metal salts* (*ca*. 1 mmol) (25 ml) was mixed with ethanolic solution of Hcpt (*ca*. 1.5 mmol) (25 ml). mixture was refluxed for 2-4 h. The respective sulfides Ag_2S (black), CuS (black), PbS (black), Hg_2S (black) and CdS (yellow) were precipitated and characterized after separation. The filtrat thus obtained was evaporated to dryness, the resultant residue wa crystallized from chloroform. These crystals were recrystallized from CCl_4/ethyl acetate (1:1). The resulting crystals were chara terized as N-carboethoxy-1-pyrroleamide. Abstraction of sulfur b soft metal ions from similar ligands was earlier reported from ou laboratory.[1-3]

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*$AgNO_3$, $CuCl_2.2H_2O$, $Pb(NO_3)_2$, $HgCl_2$ and $CdSO_4.4H_2O$.

III.2 RESULTS AND DISCUSSION

All compounds are air stable, insoluble in non-coordinating solvents and soluble in solvents like ethanol, DMF, DMSO, acetone etc. Analytical data (Table III.1) are in good agreement with the stoichiometry proposed for the complexes. Metal ions form inner complexes (b-g) rather than simple salts (a). Hcpt functions both as a mono and bidentate ligand.

III.2.1 Reactions

The complexation reactions of metal salts with the ligand (Hcpt) can be described by following equations:

$$\text{Metal chloride} + 2\ \text{Hcpt} \longrightarrow M(II)(cpt)_2 + 2\ HCl \qquad .. (1)$$

(metal chloride = $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $PdCl_2.2H_2O$, H_2PtCl_6)

$$MCl_2 + 2\ \text{Hcpt} + py \longrightarrow M(cpt)_2py + 2\ HCl \qquad .. (2)$$

(M = Ni, Co)

$$AgNO_3 + \text{Hcpt} \longrightarrow \text{Agcpt} + HNO_3 \qquad .. (3)$$

$$MCl_3.3H_2O + 2\ \text{Hcpt} \longrightarrow M(cpt)_2Cl(H_2O) + 2\ HCl + 2\ H_2O \qquad .. (4)$$

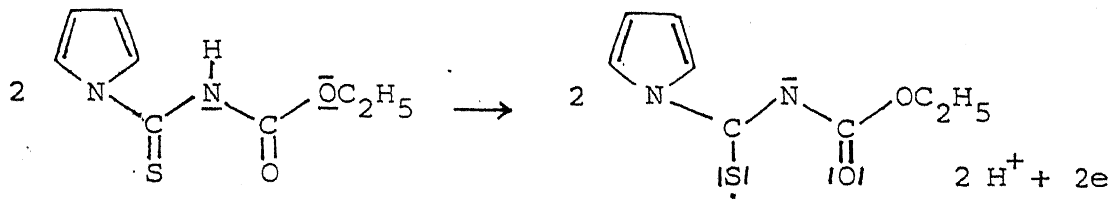
(M = Ru, Rh)

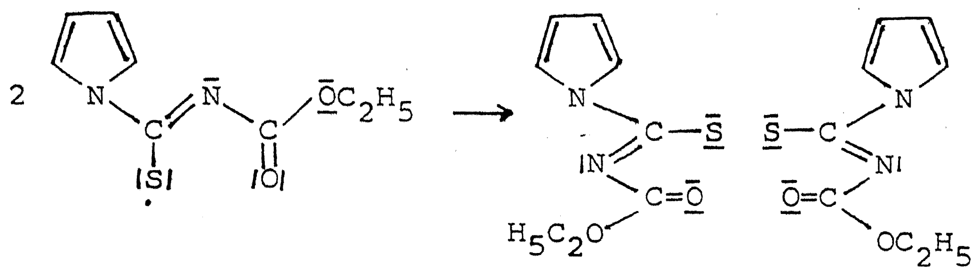
$$2\ RhCl(PPh_3)_3 + 2\ \text{Hcpt} \longrightarrow [Rh(Hcpt)(PPh_3)Cl]_2 + 4\ PPh_3 \qquad .. (5)$$

In case of H_2PtCl_6, Pt(IV) is first reduced to Pt(II) and then gets coordinated to Hcpt. Ligand itself functions as reducing

agent which in turn gets oxidised to a dimer with sulfur-sulfur bond. The dimer does not seem to involve in the complexation. The dimer has been isolated and characterized. The following equations describe the details of the reaction:

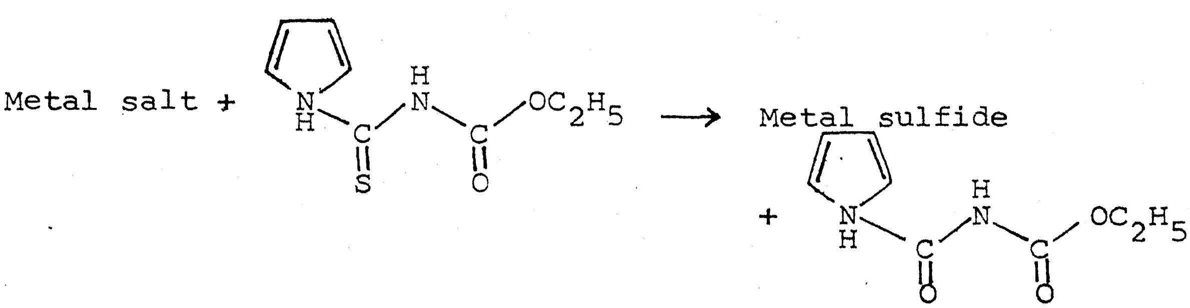
(i) $Pt(IV) + 2\ e \longrightarrow Pt(II)$

(ii) 

(iii) 

(iv) $Pt(II) + 2\ Hcpt \longrightarrow Pt(cpt)_2 + 2\ H^+$

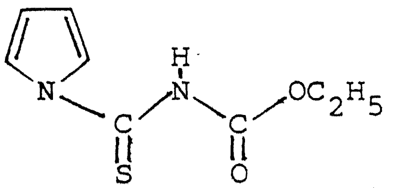
With soft metal ions, on refluxing, instead of complexation, sulfur abstraction takes place, resulting in the formation of meta sulfide and oxygenated form of the ligand according to following equation:



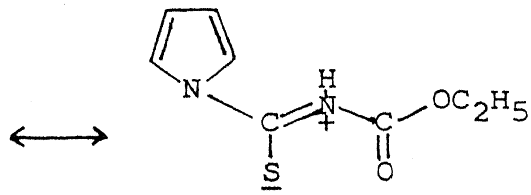
Ru(III), Rh(I) and Rh(III) complexes and others were found non-conducting in organic solvents.

III.2.2 IR spectra

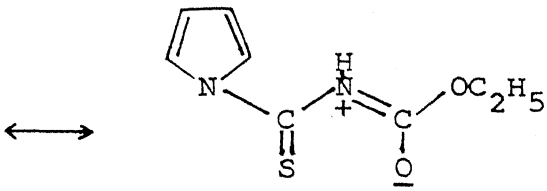
The donor ability of the ligand and the shifts of various IR bands in the spectra of complexes can be best understood in terms of resonance structures (I, II and III):



I



II



III

The ligand N-carboethoxy-1-pyrrolethioamide (Hcpt) contains a thioamide (HNCS) group which gives rise to four characteristic thioamide bands in the region of 1500, 1300, 1000 and 800 cm^{-1}. These thioamide bands namely, I, II, III and IV have principal contributions from ($\delta_{NH} + \nu_{C\cdots N}$), ($\delta_{NH} + \nu_{C\cdots N} + \delta_{C-H}$), ($\delta_{C-N} + \nu_{C=S}$) and $\nu_{C\cdots S}$ modes of vibrations, respectively.[4] The shifts in the positions of these bands is of immense help in identifying

the donor atoms.

The positions of the major bands of interest are shifted in the spectra of complexes. The changes in i r spectra and the inferences drawn regarding site of bonding are summarized below.

The band at 3210 cm^{-1} ν(NH) in the spectrum of ligand disappears in the spectra of the complexes the only exception being Rh(I) complex. This could most probably be explained on the assumption that during the formation of the complexes, the NH group of the ligand is deprotonated with the formation of a metal to nitrogen bond. Two bands at 685 and 630 cm^{-1} assigned to τ(NH) also disappear in the spectra of the complexes, confirming deproto nation of the ligand. Formation of metal-nitrogen bond is indeed confirmed by the appearance of a new band ν(M-N) in the spectra of the complexes. In case of $[RhCl(Hcpt)(PPh_3)]_2$, the ligand seems to be monodentate through carbonyl oxygen and structure III predominates. This is supported by lowering of ν(C=O). The band at 3210 cm^{-1} ν(NH) becomes broad, possibly because of hydrogen bonding in the solid state of the compound. The interpretation of changes to ν(NH) bands support (NH) to metal coordination is not always dependable. H-bonding and ion-dipole, (NH)---M interaction may also cause variation in ν(NH) behaviour. Obviously, it is sa to use the ν(NH) variation on complexation in conjunction with other i.r. shifts. At the same time thioamide band I, II and IV al undergo blue shift by 40, 10 and 10 cm^{-1}, respectively. This increase indeed is expected in case of coordination through carbonyl oxygen. Thioamide band III, unexpectedly goes down by 35 cm^{-1}

The broad band around 3300-3500 cm^{-1} and 1630 cm^{-1} in the spectra of Ru(III) and Rh(III) complexes are tentatively assigned to stretching (symmetric and asymmetric) and bending modes of water molecules, respectively.

For Ni(II), Co(II) and Cu(II) structure I and III seem to predominate and the band at 1730 cm^{-1} ν(C=O) of Hcpt shifts towards lower wave numbers (Table III.2). A band at 1125 cm^{-1} of Hcpt ν (C=S) either remains stationary or goes up and thioamide band IV having major contribution of ν(C=S) (ca. 880 cm^{-1}) undergoes blue shifts in the spectra of complexes. These shifts are indicative of non-involvement of thiocarbonyl sulfur in bond formation, indicating strong interaction of the metal ion with caronyl oxygen.

For Ag(I), Rh(III), Pt(II), Pd(II) and Ru(III) complexes structure I and II of the ligand appear to be operative and the band due to ν(C=O) at 1730 cm^{-1} in the ligand either remains stationary or shifts towards higher wave number. This indicates the non-involvement of carbonyl oxygen in the bond formation with the metal ion. The ν(C=S) band of the ligand at 1125 cm^{-1} shifts to lower frequencies whereas in case of $[RuCl(cpt)_2(H_2O)]$ the band disappears probably merging with 1095 cm^{-1} bands of the ligand. The red shift observed for thioamide band IV further supports the bonding through thiocarbonyl sulfur.

The band at 1500 cm^{-1} in the ligand is assigned to thioamide band I ($\nu_{C\cdots N}$ + δ_{N-H}).[5] In most of the complexes this band

shifts to higher wave numbers (Table III.2). Only in the case of $Cu(cpt)_2$ the band remains stationary.

Thioamide band I undergoes red shift because of formation of metal-nitrogen bond whereas bonding through oxygen or sulfur will cause blue shift. Obviously the two shifts are in the opposite directions. In case of simultaneous coordination through nitrogen and oxygen or sulfur atoms, higher value for thioamide band I indicates relatively stronger interaction of the metal ion with carbonyl oxygen or thiocarbonyl sulfur as compared to nitrogen. If, thioamide band I undergoes red shift, just the opposite statement will hold good. In such situation shifts should be small. In case of $Cu(cpt)_2$ the two shifts are exactly balanced.

A band at 1320 cm^{-1} of Hcpt assigned to thioamide band II ($\delta_{CH} + \nu_{C-N} + \delta_{N-H}$) shifts to lower frequencies (ca. 10-12 cm^{-1}) in the spectra of all the complexes with the exception of $[RhCl(Hcpt)(PPh_3)]_2$ in which Hcpt is bonded to rhodium(I) through carbonyl oxygen only, as expected, this band shifts to higher wave number (1330 cm^{-1}).

Thioamide band III (mainly due to ν(C=S) and ν(C-N) at 1015 cm^{-1} of Hcpt undergoes red shift on complexation in all the cases.

The new band at 1580 cm^{-1} of $[Cu(cpt)_2]$ which has been tentatively assigned to ν(C=N) will have significant contribution of ν(C=O) also as in this complex ν(C=O) of ligand at 1730 cm^{-1} disappears. Large red shift is indicative of relatively stronger

interaction of Cu(II) ion with carbonyl oxygen. As a consequence of this ν(C=O) goes down on complexation appreciably resulting in its merger with a ν(C=N) band at 1550 cm^{-1}. In case of [Ni(cpt)$_2$-(py)] band at 1580 cm^{-1} has major contribution of ν(C=N) because there is a band at 1620 cm^{-1} which is assigned as ν(C=O) in the complex. The bands at 1450 cm^{-1} and 1490 cm^{-1} for [Cu(cpt)$_2$] and [Ni(cpt)$_2$(py)], respectively have been assigned to ν(N-C=S).[6] The weak broad band at ca. 3500 cm^{-1} in the spectra of [Ni(cpt)$_2$(py)] and [Co(cpt)$_2$(py)] are characteristic of pyridine, ca. 80 cm^{-1} towards higher frequency (pyridine band at ca. 3420 cm^{-1}). In both the complexes bands in free pyridine at 604 cm^{-1} (in plane-ring deformation) and 405 cm^{-1} out-of-plane ring deformation) shifts to higher frequencies (ca. 35 cm^{-1}).[7-9]

The appearance of new medium intensity bands in the region 500-300 cm^{-1} is strong evidence of coordination by both nitrogen and oxygen or sulfur. They have been tentatively assigned to coupled vibration of ν(M-N), ν(M-O) and ν(M-S). Bands of a new representative compounds in this region are given below:
330 cm^{-1}, 345 cm^{-1} [Cu(cpt)$_2$], 335, 360 cm^{-1} [RuCl(cpt)$_2$H$_2$O], 340, 450, 490 cm^{-1} [Ni(cpt)$_2$], and 300, 390, 440 cm^{-1} [Co(cpt)$_2$-(py)].

III.2.3 Magnetic Properties

All compounds except Ni(II), Co(II), and Ru(III) complexes were found diamagnetic at room temperature. The magnetic moment

of Ni(II) complex corresponds to two unpaired electrons whereas those of Co(II) and Ru(III) indicate the presence of one unpaired electron in each.

III.2.4 Electronic Spectra

The electronic spectrum of Hcpt in ethanol exhibits two strong transitions at 300 nm and 262 nm which are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand transitions, respectively. Usually $n \rightarrow \pi^*$ transitions involving N and S occur at lower energy and are less intense than $\pi \rightarrow \pi^*$.[10,11] The spectra of almost all the compounds show the presence of these two bands with the hypsochromic blue shift. The high intensity of these bands suggest that they should be charge transfer or intraligand and not d-d transition bands. The absence of band around 300 nm ($n \rightarrow \pi^*$) from the spectra of some complexes may be due to stabilization of the energy of the lone pair of the electrons on complex formation,[12] and similarly the hypsochromic shift in bands in the spectra of complexes may be explained as metal ions are bonded through thiocarbonyl sulfur, carbonyl oxygen and nitrogen.[13] The bond formations lower the energy of non-bonding orbitals as well as π-levels, thus now more energy will be required to promote the electron from n or π level to π^* orbital hence the observed hypsochromic shift.

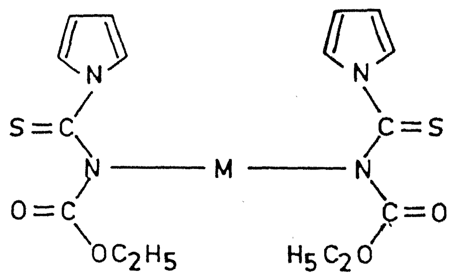
The i r evidence clearly indicates that the ligand acts as NO/NS donor in these complexes. Square planar geometry is

assigned to Ni(II), Pd(II), Pt(II), Rh(I) and Cu(II) complexes. Ru(III) and Rh(III) complexes are octahedrally coordinated whereas $[Ni(cpt)_2(py)]$ and $[Co(cpt)_2(py)]$ are proposed to have square pyramidal geometry and the Ag(cpt) complex is linear one. In case the ligand functions as a bidentate to one metal ion, it will result in four membered chelate ring (structure b) and this will involve undue strain specially in case when the ligand acts as a NO donor. In view of the above facts and the insolubility of the complexes in most of the non-coordinating solvents the complexes may have open polymeric structures with the nitrogen and oxygen atoms of one ligand being bound to two different metal atoms (structure c). It is known that OS donor β-thioxoketonates form exclusively cis-complexes with square planar coordinated metal ions and facial complexes with octahedrally coordinated metal ions.[14] Consequently, it is suggested that the Pd(II) and Pt(II) complexes (in which the ligand is NS donor have the cis-square planar configuration and those of Ru(III) and Rh(III) are octahedral. Although these structures contain a four membered ring, they do not involve undue strain because of the large size of the sulfur atom. Four membered chelate rings are known with NS ligands.[15] Hence, inspite of insolubility of compounds, in case of NS donor situation, both chelate and polymeric structures (structures d and e) are equally probable.

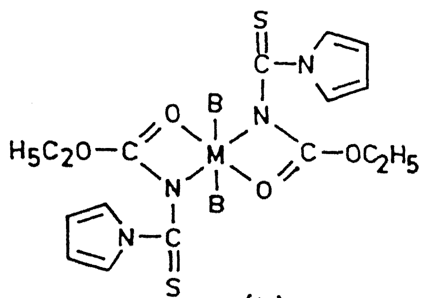
Thus, on the basis of analytical, spectral and magnetic measurement data, the following tentative geometries have been

assigned to the complexes.

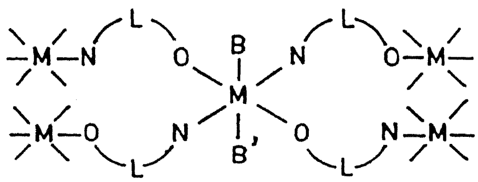
$[Cu(cpt)_2]$, $[Ni(cpt)_2]$, $[Pd(cpt)_2]$, $[Pt(cpt)_2]$	Square planar (cis)
$[RuCl(cpt)_2(H_2O)]$ and $[RhCl(cpt)_2(H_2O)]$	Octahedral
$[Ni(cpt)_2(py)][Co(cpt)_2(py)]$	Square pyramidal
$[RhCl(Hcpt)(PPh_3)]_2$	Square planar (dimeric)
$[Ag(cpt)]$	Linear (polymeric)



(a)



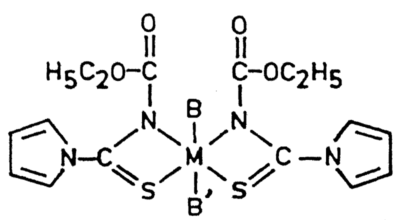
(b)



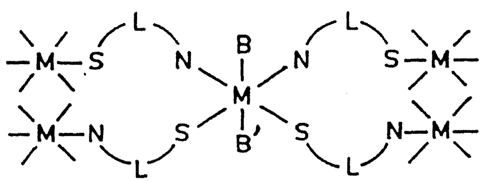
(c)

$M = Cu(II),\ Ni(II)$; $B, B' =$ nil

$M = Ni(II),\ Co(II)$; $B =$ Py, $B' =$ nil



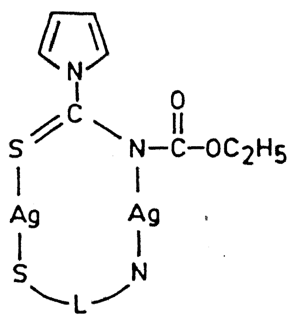
(d)



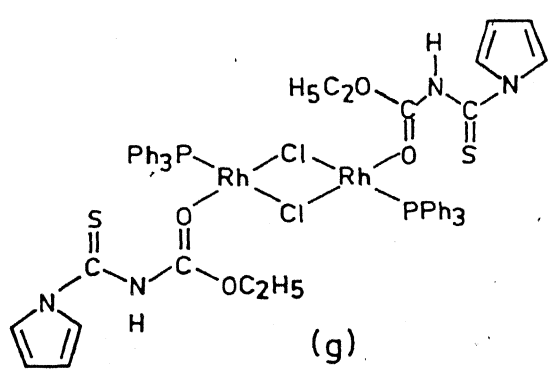
(e)

$M = Pd(II),\ Pt(II)$; $B, B' =$ nil

$M = Rh(III),\ Ru(III)$; $B = Cl$, $B' = H_2O$



(f)



(g)

Table III.1 Analytical and Magnetic Data

Compound	Colour	M.P.‡ (^{o}C)	Yield (%)	Analysis: Found (Calcd.), % M	S	Cl	C	H	N	μ_{eff} (B.M.)
1	2	3	4	5	6	7	8	9	10	11
$[Cu(cpt)_2]$	Light Brown	105	50	13.6 (13.8)	13.7 (14.0)	-	42.2 (42.0)	3.8 (4.0)	11.9 (12.2)	DM
$[Ni(cpt)_2py]$	Green	52	50	11.3 (10.9)	11.8 (12.0)	-	47.2 (47.4)	4.5 (4.3)	13.3 (13.2)	3.14
$[Ni(cpt)_2]$	Yellow	56	54	12.6 (12.8)	13.8 (14.2)	-	42.8 (42.4)	3.8 (4.0)	12.2 (12.4)	DM
$[Co(cpt)_2py]$	Brown	82	52	11.2 (10.9)	11.5 (12.0)	-	47.1 (47.4)	4.7 (4.3)	13.1 (13.2)	2.10
$[Ag(cpt)]$	Yellow	158d	80	35.3 (35.4)	10.2 (10.5)	-	31.4 (31.5)	2.6 (3.0)	9.3 (9.2)	DM
$[RuCl(cpt)_2(H_2O)]$	Black Brown	>240	56	-	12.0 (11.7)	6.8 (6.5)	35.2 (35.0)	3.2 (3.3)	10.5 (10.2)	1.64
$[RhCl(cpt)_2(H_2O)]$	Reddish Brown	238d	60	-	11.7 (11.6)	6.7 (6.4)	34.8 (34.9)	3.6 (3.3)	10.5 (10.2)	DM
$[RhCl(Hcpt)(PPh_3)]_2$	Yellow	120	70	-	5.1 (5.3)	5.7 (5.9)	52.4 (52.1)	4.5 (4.2)	4.5 (4.7)	DM

...contd.

Table III.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11
$[Pd(cpt)_2]$	Yellow	280d	65	20.8	12.5	-	38.7	3.4	10.9	DM
				(21.2)	(12.2)		(38.4)	(3.6)	(11.2)	
$[Pt(cpt)_2]$	Dark Brown	200d	48	32.7	10.6	-	32.9	3.4	9.6	DM
				(33.1)	(10.9)		(32.6)	(3.0)	(9.5)	

‡ Melting points are uncorrected ; d = decomposed

* μ_{eff} was taken at room temperature

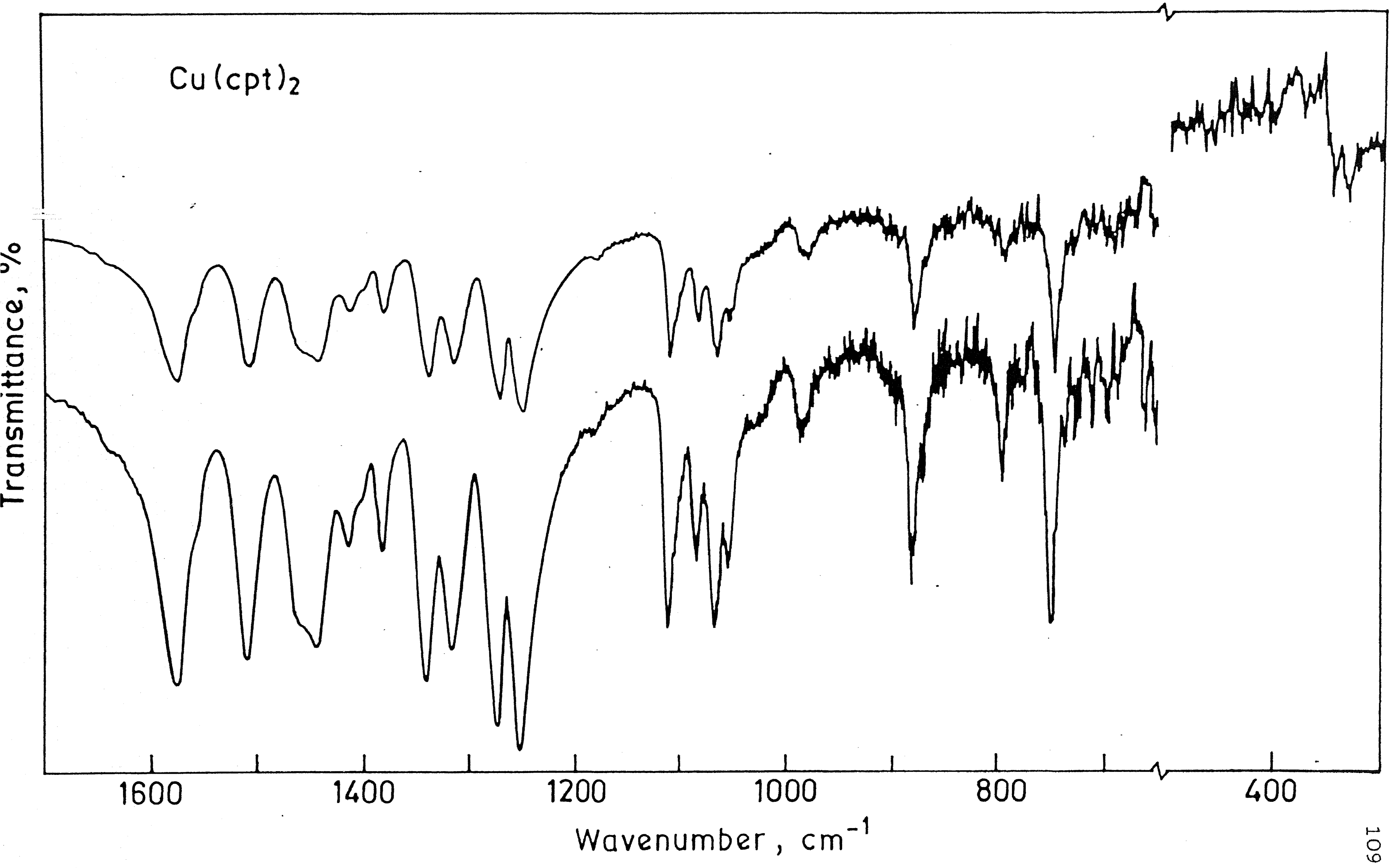
Table III.2 Major i.r. Bands of Interest. Comparison of i.r. Spectra of the Complexes with Ligand (cm^{-1})

Compound	ν(NH)	ν(C=O)	ν(C=S)	Thioamide bands				Possible coordination
				I	II	III	IV	
[Hcpt]	3210m	1730s	1125s	1500s	1320s	1015s	880s	-
[$Cu(cpt)_2$]	-	1580s*	1125m	1500s	1320s	990m	880m	N and O
[$Ni(cpt)_2py$]	-	1620s	1160m	1550s	1310s	980m	900m	N and O
[$Ni(cpt)_2$]	-	1610s	1140s	1540s	1310s	980s	900m	N and O
[$Co(cpt)_2py$]	-	1600s	1160m	1550m	1310s	990m	910s	N and O
[Ag(cpt)]	-	1750s	1120m	1550s	1300s	980s	850s	N and S
[$RuCl(cpt)_2H_2O$]	-	1750s	-	1540s	1300s	980s	850s	N and S
[$RhCl(cpt)_2H_2O$]	-	1750	1110s	1550s	1300s	990s	850s	N and S
[$RhCl(Hcpt)(PPh_3)]_2$	3300br	1650s	1140m	1540s	1330s	980s	890s	O
[$Pd(cpt)_2$]	-	1760s	1120s	1540s	1300s	980s	860s	N and S
[$Pt(cpt)_2$]	-	1765s	1115s	1550s	1300s	985s	860s	N and S

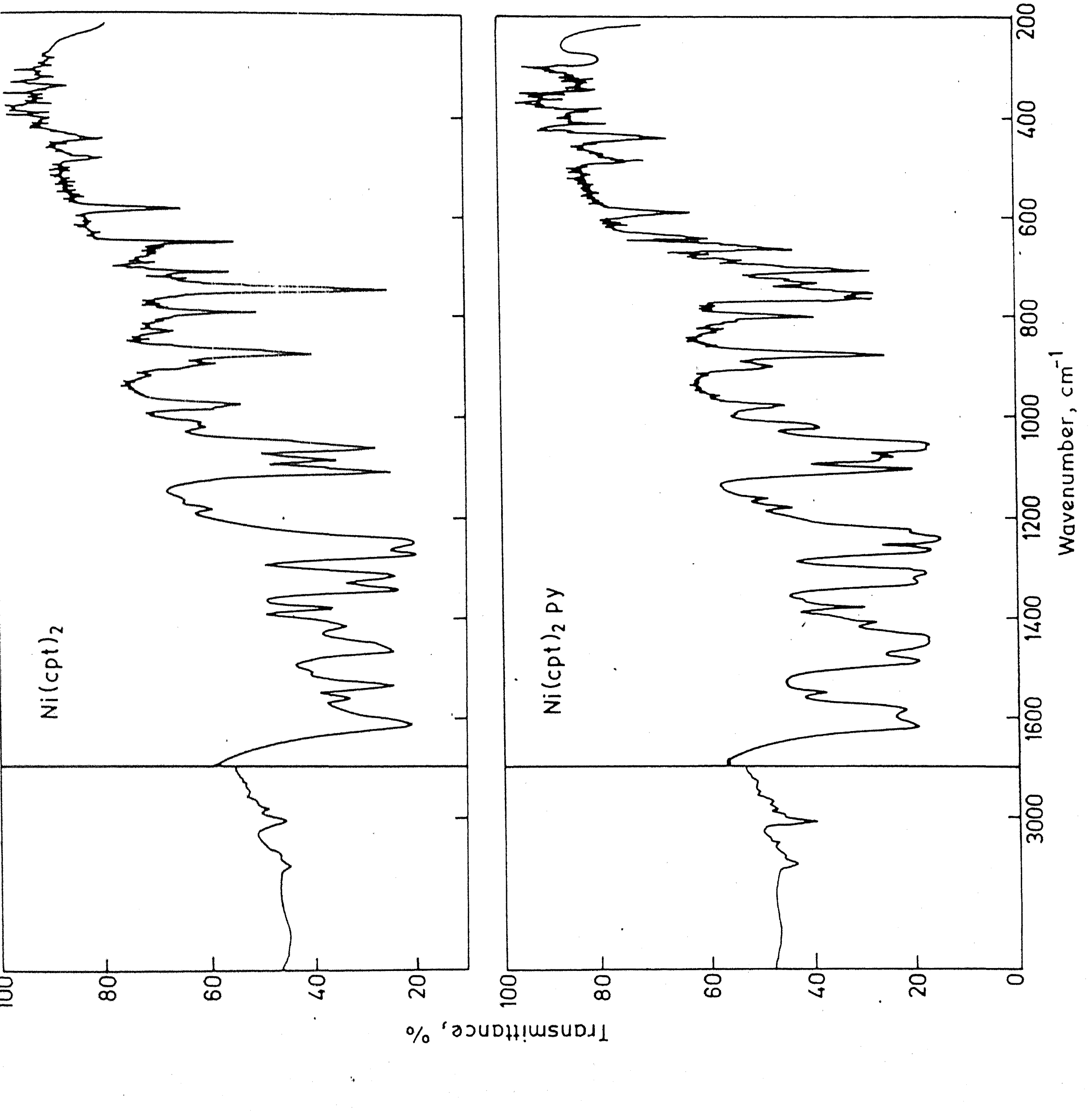
* This band has significant contribution from both ν(C=N) and ν(C=O).

Table III.3 Electronic Spectra of Ligand and Complexes in 95% Ethanol

Compound	Band position λ_{max} (nm)	Assignments
Ligand [Hcpt]	262	$\pi \rightarrow \pi^*$
	300	$n \rightarrow \pi^*$
$[Cu(cpt)_2]$	285	IL
$[Ni(cpt)_2py]$	285	IL
	320	IL
$[Ni(cpt)_2$	280	IL
	360	IL
$[Co(cpt)_2py]$	285	IL
	320	IL
$[Ag(cpt)]$	280	IL
	350	IL
$[RuCl(cpt)_2H_2O]$	265	CT or IL
	320	IL
	425	${}^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$
$[RhCl(cpt)_2H_2O]$	280	IL
	320	IL
$[RhCl(Hcpt)(PPh_3)]_2$	280	IL
	320	IL
$[Pd(cpt)_2]$	250	CT
	285	IL
	325	IL
	400	$d_{x^2-y^2} \rightarrow d_{xy}$ $({}^1A_{1g} \rightarrow {}^1B_{1g})$
$[Pt(cpt)_2]$	295	IL
	450	$d_{x^2-y^2} \rightarrow d_{xy}$ $({}^1A_{1g} \rightarrow {}^1B_{1g})$

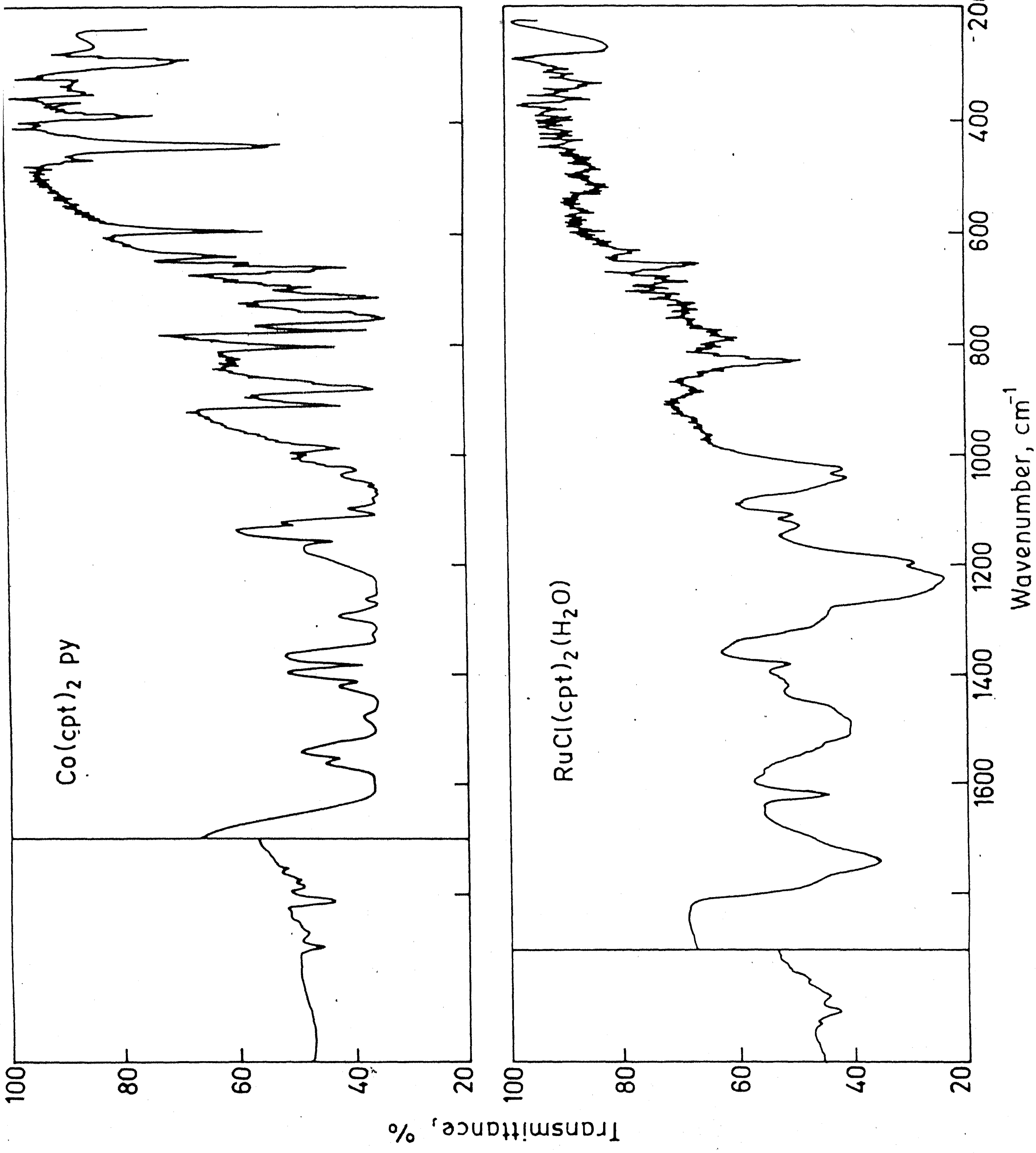


Cu(cpt)₂
Transmittance, %
1600
1400
1200
1000
800
400
Wavenumber, cm⁻¹

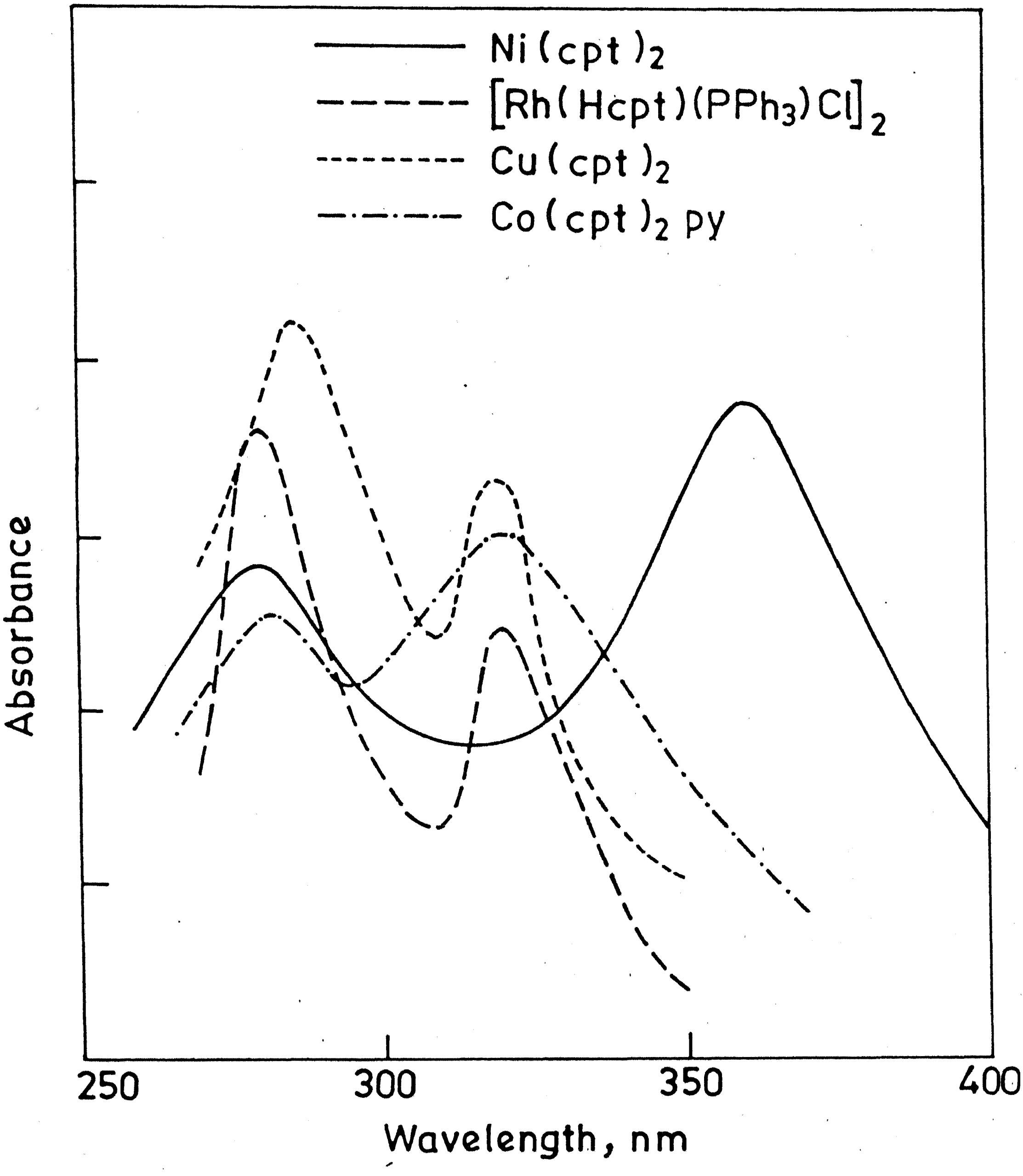


Ni(cpt)2
Ni(cpt)2 Py
Transmittance, %
Wavenumber, cm-1
100
80
60
40
20
0
3000
1600
1400
1200
1000
800
600
400
200

Fig. III.2



Co(cpt)$_2$ py
RuCl(cpt)$_2$(H$_2$O)
Transmittance, %
100
80
60
40
20
Wavenumber, cm^{-1}
1600
1400
1200
1000
800
600
400
200



Ni(cpt)$_2$
[Rh(Hcpt)(PPh$_3$)Cl]$_2$
Cu(cpt)$_2$
Co(cpt)$_2$ py
Absorbance
250
300
350
400
Wavelength, nm

Fig. III.4

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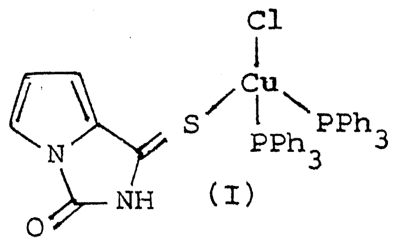
CHAPTER IV

REACTIONS OF $[Cu^{I}(MPh_3)_3X]$ ($M = P$ or As; $X = Cl^-$, Br^- or I^-) WITH SOME AROMATIC THIOAMIDES*

This chapter describes the reactions of variety of aromatic thioamides (ArCSNHCOR) with $[Cu^{I}(MPh_3)_3X]$. The reaction products have been isolated as dark coloured solids and characterized using analytical, spectral and magnetic data. The single crystal X-ray diffraction analysis of one of the copper(I) complexes shows tetrahedral coordination with the aromatic ligand to copper via the thiocarbonyl sulphur (I):



(I)

All other copper(I) complexes have similar mode of bonding and stereochemistry.

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*Transition Met. Chem., 11, 223 (1986).
Transition Met. Chem., 11, ~~000~~ 403 (1986).

IV.1 EXPERIMENTAL

The complexes of the type $[Cu(MPh_3)_3X]$[1,2] (M = P or As; X Cl^-, Br^- or I^-) and the ligands N-carboethoxy-4-toluenethioamide (Hctt), N-carboethoxy-2-pyrrolethioamide (Hcept), N-carboethoxy-1-pyrrolethioamide (Hcpt), 2-thiopyrrole-1,2-dicarboximide (Htp) and N-carboamido-2-pyrrolethioamide (Hcapt) were prepared by literature methods (see Appendix). Copper, phosphorus, chloride and sulfur were determined gravimetrically. Instruments used were same as described in earlier chapters.

IV.1.1 Preparation of Complexes

(i) (N-Carboethoxy-4-toluenethioamide)chloro(bistriphenylphosphine)copper(I)

Hctt (0.23 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[Cu(PPh_3)_3Cl]$ (0.88 g, 1 mmol) in benzene (25 ml) at room temperature. The red solution thus obtained was refluxed for 0.5 hrto 1 hr volume reduced to half, which on addition of petroleum ether (10 ml) gave red crystals. The red crystalline compound was filtered, washed with petroleum ether and dried *in vacuo*.

(ii) Bromo(N-carboethoxy-4-toluenethioamide)(bistriphenylphosphine)copper(I)

Hctt (0.23 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuBr(PPh_3)_3]$ (0.93 g, 1 mmol) in benzene (25 ml) at room

temperature. The red solution thus obtained was refluxed for 0.5 hr to 1 hr volume reduced to half, which on addition of petroleum ether (10 ml) gave red crystals. The crystals were filtered, washed with petroleum ether and dried *in vacuo*.

(iii) (N-Carboethoxy-4-toluenethioamide)iodo(bistriphenylphosphine)copper(I)

Hctt (0.23 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuI(PPh_3)_3]$ (0.98 g, 1 mmol) in benzene (25 ml) at room temperature. The red solution thus obtained was refluxed for 0.5 hr to 1 hr volume reduced to half, which on addition of petroleum ether (10 ml) gave red crystals , which were filtered, washed with petroleum ether and dried *in vacuo*.

(iv) (N-Carboethoxy-4-toluenethioamide)chloro(bistriphenylarsine)-copper(I)

Hctt (0.23 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuCl(AsPh_3)_3]$ (1.02 g, 1 mmol) in benzene (25 ml) at room temperature. The dark orange solution thus obtained was refluxed 0.5 hr to 1 hr, volume reduced to half, which on addition of petrole ether (10 ml) gave dark orange crystals. The orange crystals were filtered, washed with petroleum ether and dried *in vacuo*.

(v) Bromo(N-carboethoxy-4-toluenethioamide)(bistriphenylarsine) copper(I)

Hctt (0.23 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuBr(AsPh_3)_3]$ (1.06 g, 1 mmol) in benzene (25 ml) at room

temperature. The orange solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half. Addition of petroleum ether (10 ml) gave orange crystals which were filtered, washed with petroleum ether and dried *in vacuo*.

(vi) (N-Carboethoxy-4-toluenethioamide)iodo(bistriphenylarsine)-copper(I)

Hctt (0.23 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuI(AsPh_3)_3]$ (1.10 g, 1 mmol) in benzene (25 ml) at room temperature. The orange solution thus obtained was refluxed for 0.5 hr to 1 hr, and the volume reduced to half. Addition of petroleum ether (10 ml) gave orange crystals which were filtered, washed with petroleum ether and dried *in vacuo*.

(vii) (N-Carboethoxy-2-pyrrolethioamide)chloro(bistriphenylphosphine)copper(I)

Hcept (0.20 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuCl(PPh_3)_3]$ (0.88 g, 1 mmol) in benzene (25 ml) at room temperature. The orange solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half and added petroleum ether (10 ml) which gave orange crystals. Filtered, washed with petroleum ether and dried *in vacuo*.

(viii) Bromo(N-carboethoxy-2-pyrrolethioamide)(bistriphenylphosphine)copper(I)

Hcept (0.20 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuBr(PPh_3)_3]$ (0.93 g, 1 mmol) in benzene (25 ml) at room

temperature. The orange solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half and added petroleum ether (10 ml) which gave orange crystals. Filtered, washed with petroleum ether and dried _in vacuo_.

(ix) (N-Carboethoxy-2-pyrrolethioamide)iodo(bistriphenylphosphine)copper(I)

Hcept 90.20 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuI(PPh_3)_3]$ (0.98 g, 1 mmol) in benzene (25 ml) at room temperature. The orange solution thus obtained was refluxed for 0.5 hr to 1 hr, reduce to half and added petroleum ether (10 ml) which gave orange crystals. Filtered, washed with petroleum ether and dried _in vacuo_.

(x) (N-Carboethoxy-2-pyrrolethioamide)chloro(bistriphenylarsine)-copper(I)

Hcept (0.20 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuCl(AsPh_3)_3]$ (1.02 g, 1 mmol) in benzene (25 ml) at room temperature. The maroon solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half, added petroleum ether (10 ml) which gave maroon crystals. Filtered, washed with petroleum ether and dried _in vacuo_.

(xi) Bromo(N-carboethoxy-2-pyrrolethioamide)(bistriphenylarsine)-copper(I)

Hcept (0.20 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuBr(AsPh_3)_3]$ (1.06 g, 1 mmol) in benzene (25 ml) at room

temperature. The maroon solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half, on addition of petroleum ether (10 ml) gave maroom crystals. Filtered, washed with petroleum ether and dried in vacuo.

(xii) (N-carboethoxy-2-pyrrolethioamide)iodo(bistriphenylarsine)-copper(I)

Hcept (0.20 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuI(AsPh_3)_3]$ (1.10 g, 1 mmol) in benzene (25 ml) at room temperature. The maroon solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half and added petroleum ether (10 ml) which gave maroon crystals. Filtered, washed with petroleum ether and dried in vacuo.

(xiii) (N-Carboethoxy-1-pyrrolethioamide)chloro(bistriphenyl-phosphine)copper(I)

Hcpt (0.20 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuCl(PPh_3)_3]$ (0.88 g, 1 mmol) in benzene (25 ml) at room temperature. The yellow solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half, added petroleum ether (10 ml) to give yellow crystals. Filtered, washed with petroleum ether and dried in vacuo.

(xiv) Bromo(N-carboethoxy-1-pyrrolethioamide)(bistriphenyl-phosphine)copper(I)

Hcpt (0.20 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuBr(PPh_3)_3]$ (0.93 g, 1 mmol) in benzene (25 ml) at room

temperature. The yellow solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half, added petroleum ether (10 ml) to give yellow crystals. Filtered, washed with petroleum ether and dried in vacuo.

(xv) (N-Carboethoxy-1-pyrrolethioamide)chloro(bistriphenyl-arsine)copper(I)

Hcpt (0.20 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuCl(AsPh_3)_3]$ (1.02 g, 1 mmol) in benzene (25 ml) at room temperature. The yellow solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half, added petroleum ether (10 ml) to give yellow crystals. Filtered, washed with petroleum ether and dried in vacuo.

(xvi) Bromo(N-carboethoxy-1-pyrrolethioamide)(bistriphenyl-arsine)copper(I)

Hcpt (0.20 g, 1 mmole in benzene (25 ml) was mixed slowly with $[CuBr(AsPh_3)_3]$ (1.06 g, 1 mmol) in benzene (25 ml) at room temperature. Yellow solution thus obtained was refluxed for 0.5 h to 1 hr, reduced to half, added petroleum ether (10 ml) to give yellow crystals. Filtered, washed with petroleum ether and dried in vacuo.

(xvii) (2-Thiopyrrole-1,2-dicarboximide)chloro(bistriphenyl-phosphine)copper(I)

Htp (0.16 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuCl(PPh_3)_3]$ (0.88 g, 1 mmol) in benzene (25 ml) at room

temperature. The dark red solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half and addition of petroleum ether (10 ml) gave dark red crystals. Filtered, washed with petroleum ether and dried in vacuo.

(xviii) Bromo(2-thiopyrrole-1,2-dicarboximide)(bistriphenylphosphine)copper(I)

Htp (0.16 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuBr(PPh_3)_3]$ (0.93 g, 1 mmol) in benzene (25 ml) at room temperature. The dark red solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half. On addition of petroleum ether (10 ml) gave dark red crystals, which were filtered, washed with petroleum ether and dried in vacuo.

(xix) Iodo(2-thiopyrrole-1,2-dicarboximide)(bistriphenylphosphine)copper(I)

Htp (0.16 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuI(PPh_3)_3]$(0.98 g, 1 mmol) in benzene (25 ml) at room temperature. The dark red solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half, and on addition of petroleum ether (10 ml) gave dark red crystals. These were filtered, washed with petroleum ether and dried in vacuo.

(xx) Chloro(2-thiopyrrole-1,2-dicarboximide)(bistriphenylarsine)-copper(I)

Htp (0.16 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuCl(AsPh_3)_3]$ (1.02 g, 1 mmol) in benzene (25 ml) at room

temperature. The dark red solution thus obtained was refluxed for 0.5 hr to 1 hr. The solution reduced to half, which on adding petroleum ether (10 ml) gave brown crystals. Filtered, washed with petroleum ether and dried in vacuo.

(xxi) Bromo(2-thiopyrrole-1,2-dicarboximide)(bistriphenylarsine)-copper(I)

Htp (0.16 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuBr(AsPh_3)_3]$ (1.06 g, 1 mmol) in benzene (25 ml) at room temperature. The reddish brown solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half. Addition of petroleum ether (10 ml) gave reddish brown crystals. Filtered, washed with petroleum ether and dried in vacuo.

(xxii) Iodo(2-thiopyrrole-1,2-dicarboximide)(bistriphenylarsine)-copper(I)

Htp (0.16 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuI(AsPh_3)_3]$ (1.10 g, 1 mmol) in benzene (25 ml) at room temperature. The reddish brown solution thus obtained was refluxed for 0.5 hr to 1 hr, reduce to half. Addition of 10 ml of petroleum ether gave reddish brown crystals which were filtered, washed with petroleum ether and dried in vacuo.

(xxiii) (N-Carboamido-2-pyrrolethioamide)chloro(bistriphenyl-phosphine)copper(I)

Hcapt (0.17 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuCl(PPh_3)_3]$ (0.88 g, 1 mmol) in benzene (25 ml) at room

temperature. The yellow solution thus obtained was refluxed for 0.5 hr to 1 hr,solution was reduced to half and on addition of petroleum ether (10 ml) gave yellow crystals. Filtered, washed with petroleum ether and dried in vacuo.

(xxiv) Bromo(N-carboamido-2-pyrrolethioamide)(bistriphenylphosphine)copper(I)

Hcapt (0.17 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuBr(PPh_3)_3]$ (0.93 g, 1 mmol) in benzene (25 ml) at room temperature. The yellow solution thus obtained was refluxed for 0.5 hr to 1 hr, solution reduced to half, which on addition of petroleum ether (10 ml), gave yellow crystals. Filtered, washed with petroleum ether and dried *in vacuo*.

(xxv) (N-Carboamido-2-pyrrolethioamide)iodo(bistriphenylphosphine)copper(I)

Hcapt (0.17 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuI(PPh_3)_3]$ (0.98 g, 1 mmol) in benzene (25 ml) at room temperature. The yellow solution thus obtained was refluxed for 0.5 hr to 1hr,reduced to half and on addition of petroleum ether (10 ml) gave yellow crystals. Filtered, washed with petroleum ether and dried *in vacuo*.

(xxvi) (N-Carboamido-2-pyrrolethioamide)chloro(bistriphenylarsine)copper(I)

Hcapt (0.17 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuCl(AsPh_3)_3]$ (1.02 g, 1 mmol) in benzene (25 ml) at room

temperature. The brown solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half, added petroleum ether (10 ml) to give brown crystals. Filtered, washed with petroleum ether and dried *in vacuo*.

(xxvii) Bromo(N-carboamido-2-pyrrolethioamide)(bistriphenylarsine)copper(I)

Hcapt (0.17 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuBr(AsPh_3)_3]$ (1.06 g, 1 mmol) in benzene (25 ml) at room temperature. The brown solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half, added petroleum ether (10 ml) to give brown crystals. Filtered, washed with petroleum ether and dried *in vacuo*.

(xxviii) (N-Carboamido-2-pyrrolethioamide)iodo(bistriphenylarsine)copper(I)

Hcapt (0.17 g, 1 mmol) in benzene (25 ml) was mixed slowly with $[CuI(AsPh_3)_3]$ (1.10 g, 1 mmol) in benzene (25 ml) at room temperature. The brown solution thus obtained was refluxed for 0.5 hr to 1 hr, reduced to half, added petroleum ether (10 ml) to give brown crystals. Filtered, washed with petroleum ether and dried *in vacuo*.

Analogous Cu(I) complexes with N-carboethoxy-2-thiophenethioamide and N-carbophenylamido-2-pyrrolethioamide could not be obtained under similar experimental conditions. N-Carboethoxy-1-pyrrolethioamide did not react with $CuI(MPh_3)_3$ (M = P, As)

to give $CuI(Hcpt)(MPh_3)_2$.

IV.2 RESULTS AND DISCUSSION

IV.2.1 IR Spectra

The infrared spectra of the ligands[3,4] are very complex. The characteristic bands of the pyrrole moiety[5] in Hcept, Htp and Hcapt do not shift in the spectra of the complexes (maximum shift $\pm$ 5 cm^{-1}). This indicates the non-involvement of nitrogen atom of the pyrrole ring in bond formation. The ring nitrogen is weakly basic and the deprotonation of pyrrole can take place in highly basic media in which the ligands are not stable. It is, therefore, assumed that bonding in the complexes is with the -C(S)NHC(O)- moiety in all cases, and the major shifts in the position of the i.r. bands should be for ν(N-H), ν(C=O), ν(C=S) and four thioamide bands. The discernible ν(N-H) bands of the ligands shift only a little on complexation indicating the non-involvement of the N-H group in the coordination.

All complexes exhibit the characteristic bands of PPh_3[6] or As

$CuX(Hctt)(MPh_3)_2$ (M = P, As; X = Cl, Br, I)

A band at 3220 cm^{-1}, assigned to ν(N-H), could not be used reliably for ascertaining the bonding through nitrogen because of unsystematic shifts after complexation. The position of the band at around 1765 cm^{-1} assigned to ν(C=O), either remains stationary or shifts towards higher wave number (ca. $\Delta\nu$ 5 cm^{-1}) in the complexes ruling out coordination through the carbonyl group.

A band at 1585 cm^{-1} $\nu(C\cdots N)$ shifts to higher wave number (<u>ca</u>. $\Delta\nu$ 25-35 cm^{-1}) indicating non-involvement of nitrogen in bonding. Thioamide band I ($\nu C\cdots N + \delta NH$) shifts to lower wave numbers (<u>ca</u>. $\Delta\nu$ 10-30 cm^{-1}). Thioamide band II at 1360 cm^{-1} either remains stationary or goes up by 5-10 cm^{-1}. Position of thioamide band IV (850 cm^{-1}/830 cm^{-1}) is invariant but the band at 830 cm^{-1} appears with appreciable reduced intensity in the complexes. The band at 1130 cm^{-1} $\nu(C{=}S)$ systematically goes down (5-20 cm^{-1}) indicating bonding through sulfur.

The presence of NH in the complexes was confirmed by the ^{1}H n.m.r. spectrum in $CDCl_3$ which displayed a signal at δ 11.3 ppm (singlet, intensity 1) for the uncomplexed base, δ 11.8 ppm (s, 1, NH).[4]

The ^{31}P n.m.r. shows the two triphenylphosphines to be equivalent giving a singlet peak which is not very broad. Comparison of ^{1}H n.m.r. spectrum with that of $Cu(PPh_3)_3Cl$ shows that this complex has two triphenylphosphine molecules. ^{31}P n.m.r. was done on 250 MHz machine with the synthesizer freq. 101.265 Hz. The samples were dissolved in partially dueterated benzene. The n.m.r. was referenced to external 85% H_3PO_4 (aq.) δ 0.00 ppm with positive values of high frequencies at room temperature.

Field desorption mass spectrum (FD/MS) of $CuCl(Hctt)(PPh_3)_2$ was done in solution which shows peaks at m/e of 622, CuCl-$(PPh_3)_2$; 587, $Cu(PPh_3)_2$; 360, $CuCl(PPh_3)$; 297, $Cl(PPh_3)$; 262, PPh_3; 223, Hctt, respectively. The parent molecular ion could not be identified.

$CuX(Hcept)(MPh_3)_2$ (M = P, As; X = Cl, Br, I)

Band at 1765 cm^{-1} assigned to ν(C=O) shifts to higher frequencies (10-15 cm^{-1}) which excludes carbonyl oxygen from bond formation. Band at 1540 cm^{-1} (thioamide band I) undergoes blue shift (10-20 cm^{-1}) with the exception of $CuI(Hcept)(AsPh_3)_2$, where it remains unchanged at 1540 cm^{-1}. This observation excludes N atom as the donor site. Band at 1120 cm^{-1} assigned to ν(C=S) either goes down or disappears merging with ligand bands at lower wave numbers. Band at 870 cm^{-1} either remains unchanged or goes down. This observation supports involvement of sulfur as the donor site.

$CuX(Hcpt)(MPh_3)_2$ (M = P, As; X = Cl or Br)

The i.r. band due to ν(NH) (3210 cm^{-1}) in the free base[4] could not be detected but weak bands due to τ(NH) at 630 and 680 cm^{-1} were observed in the spectra of the complexes without any shifts. The band due to ν(C=O) (1730 cm^{-1}) either remains stationary or shifts towards higher wave number (ca. 35 cm^{-1}) after complexation of the ligand. The ν(C=S) band (1125 cm^{-1}) and the thioamide band IV [mainly due to ν(C=S), 880 cm^{-1}] shift to lower wave numbers (ca. 10 cm^{-1}). The thioamide band I [δ(NH) + ν(CN)][8] (1500 cm^{-1}) in all the complexes increases (ca. 30 cm^{-1}). From the above shifts we conclude unequivocally that copper I is bonded to the ligand through sulfur. Bonding via sulfur is also favoured because copper(I) is soft and should

prefer to interact with a soft donor such as sulfur. Tetrahedral geometry is assigned to the copper(I) complexes. A new band of weak to medium intensity in the 264-295 cm^{-1} region in the spectra of the complexes is assigned to ν(Cu-S).[9]

<u>$CuX(Htp)(MPh_3)_2$ (M = P, As; X = Cl, Br, I)</u>

Band at 3200 cm^{-1} assigned to ν(NH) becomes broad on complexation. Strong band at 1765 cm^{-1} ν(C=O) shifts to higher wave numbers (<u>ca</u>. 25-35 cm^{-1}) indicating non-involvement of carbonyl oxygen in bond formation. Thioamide band I (δNH + νC$\overset{...}{-}$N) of the ligands appears as a strong band at 1555 cm^{-1} and shifts to highe wave numbers (5-15 cm^{-1}) indicating non-involvement of nitrogen as donor site. Thioamide band II & III are not diagnostic to draw any inference. ν(C=S) at 1145 cm^{-1} and thioamide band IV at 850 cm^{-1} are practically invarient after complexation. Infrared data certainly establish the exclusion of nitrogen and oxygen as donor atoms, whereas the bond formation of Cu(I) with sulfur is not proved unequivocally, based on shifts of the i.r. bands of the ligand. According to HSAB principle of Peasson, Cu(I) being soft should preferably bind with the soft donor such as sulfur.

<u>$CuX(Hcapt)(MPh_3)_2$ (M = P, As; X = Cl, Br, I)</u>

Band at 1730 cm^{-1} either undergoes blue shifts or remains c tant which indicates the non-involvement of carbonyl oxygen in c ordination. Thioamide band I at 1540 cm^{-1} undergoes blue shift (20 cm^{-1}) indicating non-involvement of N as donor site. Band at 1

cm^{-1} ($\nu C=S$) goes down on complexation and remains constant in case $CuX(Hcapt)(AsPh_3)_2$ (X = Cl, Br, I). Band at 845 cm^{-1} (thioamide band (IV) goes down in all the cases. Above observations support the bond formation between Cu(I) and sulfur.

The free N-methyl-O-ethylthiocarbamate (MTC) absorption at 1535 cm^{-1} is assigned to thioamide I ($\delta NH + \nu C=N$) in accordance with analogous thioamides.[10,11] This band is displaced towards higher energies on coordination with thiocarbonyl sulfur. Our observations with all the aromatic thioamides are exactly identical. In complexes of analogous geometry, for instant, $[M(MTC)_3X_2]$ (M = Pd, Pt; X = Cl, Br, I), the shift depends on the halide in the order Cl $>$ Br $>$ I.[12,13] This order does not strictly holds good for $[CuX(LH)(MPh_3)_2]$ complexes reported in this chapter.

IV.2.2 Electronic Spectra

The electronic spectra of the ligands as well as the complexes were taken in dichloromethane and assigned on the basis of earlier reports.[1,14-16] The spectra of Hctt exhibit the bands at 450 nm, 310 nm and 270 nm. The higher energy band at 270 nm may be assigned to intraligand charge transfer (IL-CT) while 450 nm and 310 nm bands are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand (IL) bands, respectively. The $n \rightarrow \pi^*$ transition, usually, occur at low energy side and are less intense in comparison with $\pi \rightarrow \pi^*$ in the system involving nitrogen and sulfur

<u>Table IV.1.</u> Analytical data of the complexes

Compound	Colour	M.P. (^{o}C)	Yield (%)	Found (Calcd.), %					
				C	H	N	M	S	Halide
1	2	3	4	5	6	7	8	9	10
$[CuCl(Hctt)(PPh_3)_2]$	Red	177-179	80	66.4 (66.6)	4.9 (5.0)	1.5 (1.6)	7.4 (7.5)	3.6 (3.7)	4.2 (4.3)
$[CuBr(Hctt)(PPh_3)_2]$	Red	162-163	65	63.2 (63.3)	4.9 (4.8)	1.4 (1.6)	7.2 (7.1)	3.9 (3.6)	8.8 (9.1)
$[CuI(Hctt)(PPh_3)_2]$	Red	111-113	55	60.5 (60.2)	4.6 (4.5)	1.5 (1.5)	6.6 (6.8)	3.6 (3.4)	13.4 (13.5)
$[CuCl(Hctt)(AsPh_3)_2]$	Dark-orange	144-145	56	50.1 (50.4)	4.7 (4.6)	1.5 (1.5)	6.8 (6.8)	3.5 (3.4)	3.8 (3.8)
$[CuBr(Hctt)(AsPh_3)_2]$	Orange	110-111	49	57.5 (57.6)	4.5 (4.4)	1.3 (1.4)	6.3 (6.5)	3.4 (3.3)	8.3 (8.2)
$[CuI(Hctt)(AsPh_3)_2]$	Orange	196-197	45	54.8 (55.0)	4.3 (4.4)	1.2 (1.4)	6.4 (6.2)	3.2 (3.1)	12.5 (12.4)
$[CuCl(Hcept)(PPh_3)_2]$	Orange	155-157	82	64.2 (64.3)	5.0 (4.9)	3.5 (3.4)	7.6 (7.7)	3.7 (3.9)	4.4 (4.3)
$[CuBr(Hcept)(PPh_3)_2]$	Orange	150-152	67	61.2 (61.0)	4.6 (4.6)	3.1 (3.2)	7.2 (7.3)	3.8 (3.7)	9.4 (9.2)
$[CuI(Hcept)(PPh_3)_2]$	Orange	148-150	52	57.6 (57.9)	4.4 (4.4)	3.2 (3.1)	6.8 (7.0)	3.6 (3.5)	13.7 (13.9)

Table IV.1 (contd.)

1	2	3	4	5	6	7	8	9	10
$[CuCl(Hcept)(AsPh_3)_2]$	Maroon	126-127	56	58.2 (58.1)	4.5 (4.4)	3.2 (3.1)	6.9 (7.0)	3.6 (3.5)	3.8 (3.9)
$[CuBr(Hcept)(AsPh_3)_2]$	Maroon	169-170	54	55.1 (55.4)	4.3 (4.2)	2.8 (2.9)	6.5 (6.6)	3.5 (3.4)	8.5 (8.4)
$[CuI(Hcept)(AsPh_3)_2]$	Maroon	165-166	52	52.6 (52.7)	3.8 (4.0)	2.7 (2.8)	6.2 (6.3)	3.3 (3.2)	12.8 (12.7)
$[CuCl(Hcpt)(PPh_3)_2]$	Yellow	135	82	64.0 (64.3)	4.6 (4.9)	3.2 (3.4)	7.4 (7.7)	3.9 (3.9)	4.5 (4.3)
$[CuBr(Hcpt)(PPh_3)_2]$	Yellow	160	54	61.2 (61.0)	4.3 (4.6)	3.1 (3.2)	7.1 (7.3)	3.5 (3.7)	9.4 (9.2)
$[CuCl(Hcpt)(AsPh_3)_2]$	Yellow	70	80	57.7 (57.5)	4.0 (4.3)	3.3 (3.1)	6.7 (6.9)	3.7 (3.5)	3.6 (3.9)
$[CuBr(Hcpt)(AsPh_3)_2]$	Yellow	80	45	54.6 (54.9)	4.3 (4.2)	2.7 (2.9)	6.8 (6.6)	3.5 (3.3)	8.5 (8.3)
$[CuCl(Htp)(PPh_3)_2]$	Dark red	187	83	65.3 (65.1)	4.5 (4.4)	3.5 (3.6)	8.1 (8.2)	4.2 (4.1)	4.7 (4.6)
$[CuBr(Htp)(PPh_3)_2]$	Dark red	170	72	61.7 (61.5)	4.2 (4.1)	3.3 (3.4)	7.6 (7.7)	3.8 (3.9)	9.3 (9.2)
$[CuI(Htp)(PPh_3)_2]$	Dark red	160-161	65	58.3 (58.3)	3.8 (3.9)	3.3 (3.2)	7.2 (7.3)	3.8 (3.7)	14.7 (14.6)

...contd.

Table IV.1 (contd.)

1	2	3	4	5	6	7	8	9	10
$[CuCl(Htp)(AsPh_3)_2]$	Brown	172-174	55	58.5 (58.4)	3.9 (3.9)	3.3 (3.2)	7.2 (7.4)	3.8 (3.7)	4.2 (4.1)
$[CuBr(Htp)(AsPh_3)_2]$	Reddish brown	177-178	52	55.3 (55.5)	3.6 (3.7)	3.2 (3.1)	6.7 (7.0)	3.6 (3.5)	8.9 (8.8)
$[CuI(Htp)(AsPh_3)_2]$	Reddish brown	180-182	50	52.9 (52.8)	3.7 (3.6)	2.8 (2.9)	6.8 (6.6)	3.4 (3.4)	13.4 (13.3)
$[CuCl(Hcapt)(PPh_3)_2]$	Yellow	160d	85	63.7 (63.6)	4.7 (4.6)	5.4 (5.3)	8.2 (8.0)	4.2 (4.0)	4.6 (4.5)
$[CuBr(Hcapt)(PPh_3)_2]$	Yellow	199-200	75	60.3 (60.2)	4.3 (4.4)	5.2 (5.0)	7.7 (7.6)	4.0 (3.8)	9.7 (9.6)
$[CuI(Hcapt)(PPh_3)_2]$	Yellow	150-152	60	57.2 (57.0)	4.3 (4.2)	4.9 (4.8)	7.2 (7.1)	3.8 (3.6)	14.5 (14.4)
$[CuCl(Hcapt)(AsPh_3)_2]$	Brown	240	53	57.4 (57.3)	4.3 (4.2)	4.7 (4.8)	7.1 (7.2)	3.7 (3.6)	4.2 (4.0)
$[CuBr(Hcapt)(AsPh_3)_2]$	Brown	175-176	51	54.6 (54.5)	4.2 (4.0)	4.4 (4.5)	6.7 (6.9)	3.3 (3.5)	8.8 (8.6)
$[CuI(Hcapt)(AsPh_3)_2]$	Brown	152-153	50	54.8 (55.0)	3.7 (3.8)	4.2 (4.3)	6.4 (6.5)	3.5 (3.3)	13.2 (13.1)

Table IV.2. Major i.r. bands of ligands and complexes (cm^{-1})

Compounds	ν(NH)	ν(C=O)	ν(C=S)	Thioamide bands			
				I	II	III	IV
1	2	3	4	5	6	7	8
[Ligand(Hctt)]	3220m	1765s	1130m	1540s	1360s	1075s	850s
[CuCl(Hctt)$(PPh_3)_2$]	-	1765s	1120w	1530s	1360s	1060s	830s
[CuBr(Hctt)$(PPh_3)_2$]	-	1765s	1125w	1520s	1360s	1050s	850s
[CuI(Hctt)$(PPh_3)_2$]	-	1765s	1120w	1520m	1360s	1055s	850s
[CuCl(Hctt)$(AsPh_3)_2$]	-	1770s	1120w	1525s	1360s	1050s	850s
[CuBr(Hctt)$(AsPh_3)_2$]	-	1770s	1120w	1500s	1360s	1050s	850s
[CuI(Hctt)$(AsPh_3)_2$]	-	1770s	1110w	1500s	1360s	1060s	830s
[Ligand(Hcept)]	3350m 3325m	1765s	1120s	1540s	1340s	1070s	870m
[CuCl(Hcept)(PPh_3)]	3300w	1765s	1110m	1520s	1320m	1060s	865m
[CuBr(Hcept)$(PPh_3)_2$]	3300w	1765s	-	1520m	1320m	1050s	860m
[CuI(Hcept)$(PPh_3)_2$]	3300w	1765s	-	1510s	1320m	1050s	850m
[CuCl(Hcept)$(AsPh_3)_2$	3280w	1765s	1120m	1530s	1310s	1050s	870m
[CuBr(Hcept)$(AsPh_3)_2$]	3300w	1765s	-	1550s	1330s	1050s	860m
[CuI(Hcept)$(AsPh_3)_2$]	3320w	1765s	-	1540s	1320s	1060s	860m

...contd.

Table IV.2 (contd.)

1	2	3	4	5	6	7	8
[Ligand(Hcpt)]	3210m	1730s	1125s	1500s	1320s	1015s	880s
[CuCl(Hcpt)$(PPh_3)_2$]	-	1765s	1120s	1530s	1310s	1000s	870s
[CuBr(Hcpt)$(PPh_3)_2$]	-	1750s	1110s	1520m	1300s	1000s	850s
[CuCl(Hcpt)$(AsPh_3)_2$]	-	1770s	1120s	1520m	1320s	1010s	840s
[CuBr(Hcept)$(AsPh_3)_2$]	-	1770s	1120s	1520m	1310s	1000s	850s
[Ligand(Htp)]	3200m	1765s	1145s	1555s	1305s	1000m	850m
[CuCl(Htp)$(PPh_3)_2$]	3160w	1790s	1140m	1570s	1300m	1000m	850m
[CuBr(Htp)$(PPh_3)_2$]	3180w	1790s	1140m	1570s	1300m	1000m	850m
[CuI(Htp)$(PPh_3)_2$]	3160w	1790s	1140m	1560s	1300m	1000m	850m
[CuCl(Htp)$(AsPh_3)_2$]	3180w	1800s	1140m	1570s	1300m	1000m	850m
[CuBr(Htp)$(AsPh_3)_2$]	3160w	1800s	1140m	1560s	1300m	1000m	850m
[CuI(Htp)$(AsPh_3)_2$]	3160w	1800s	1140m	1560s	1300m	1000m	850m
[Ligand(Hcapt)]	3400, 3370, 3250	1730s	1120s	1580s	1330s	1060s	845s
[CuCl(Hcapt)$(PPh_3)_2$]	3400w 3260w	1730s	1110w	1575s	1290s	1070s	820m
[CuBr(Hcapt)$(PPh_3)_2$]	3360w 3260w	1730s	1110w	1550s	1300s	1070s	840m

...contd.

Table IV.2 (contd.)

1	2	3	4	5	6	7	8
$[CuI(Hcapt)(PPh_3)_2]$	3380w 3250w	1730s	1110w	1560s	1300w	1060s	840m
$[CuCl(Hcapt)(AsPh_3)_2]$	3400w 3260w	1730s	1120w	1580s	1300s	1070s	840m
$[CuBr(Hcapt)(AsPh_3)_2]$	3360m 3250m	1730s	1120w	1610s	1320m	1060s	840m
$[CuI(Hcapt)(AsPh_3)_2]$	3360m 3250m	1730s	1120w	1580s	1330s	1060s	840m

Table IV.3. Electronic spectra of ligands and complexes

Compounds	λ_{max} (nm)	Assignments
[Ligand(Hctt)]	450	$n \rightarrow \pi^*$
	310	$\pi \rightarrow \pi^*$
	270	CT
[$CuCl(Hctt)(PPh_3)_2$]	278	CT
	265	CT
[$CuBr(Hctt)(PPh_3)_2$]	390	$M \rightarrow L$ CT
	278	CT
	265	CT
[$CuI(Hctt)(PPh_3)_2$]	278	CT
	265	CT
[$CuCl(Hctt)(AsPh_3)_2$]	270	CT
	260	CT
[$CuBr(Hctt)(AsPh_3)_2$]	275	CT
	265	CT
[$CuI(Hctt)(AsPh_3)_2$]	300	$\pi \rightarrow \pi^*$
	275	CT
[Ligand(Hcept)]	350	$n \rightarrow \pi^*$
	292	$\pi \rightarrow \pi^*$
[$CuCl(Hcept)(PPh_3)_2$]	360	IL
	275	CT
	265	CT
[$CuBr(Hcept)(PPh_3)_2$]	360	IL
	280	CT
	275	CT
[$CuI(Hcept)(PPh_3)_2$]	355	IL
	280	$\pi \rightarrow \pi^*$
	270	CT
	260	CT

...contd.

Table IV.3 (contd.)

Compounds	λ_{max} (nm)	Assignments
[CuCl(Hcept)$(AsPh_3)_2$]	425	IL
	360	IL
	280	CT
[CuBr(Hcept)$(AsPh_3)_2$]	435	IL
	355	IL
	285	CT
[CuI(Hcept)$(AsPh_3)_2$]	435	IL
	355	IL
	275	CT
[Ligand(Hcpt)]	300	$\pi \rightarrow \pi^*$
	262	CT
[CuCl(Hcpt)$(PPh_3)_2$]	380	MLCT
	265	CT
[CuBr(Hcpt)(PPh_3)]	300	$\pi \rightarrow \pi^*$
	240	CT
[CuCl(Hcpt)$(AsPh_3)_2$]	380	MLCT
	235	
[CuBr(Hcpt)$(AsPh_3)_2$]	380	MLCT
	235	
[Ligand(Htp)]	360	$n \rightarrow \pi^*$
	330	$n \rightarrow \pi^*$
	282	$\pi \rightarrow \pi^*$
	275	CT
	265	CT

...contd.

Table IV.3 (contd.)

Compound	λ_{max} (nm)	Assignments
$[CuCl(Htp)(PPh_3)_2]$	360	$n \rightarrow \pi^*$
	325	$n \rightarrow \pi^*$
	260	CT
$[CuBr(Htp)(PPh_3)_2]$	360	$n \rightarrow \pi^*$
	320	$n \rightarrow \pi^*$
	255	CT
$[CuI(Htp)(PPh_3)_2]$	360	$n \rightarrow \pi^*$
	260	CT
$[CuCl(Htp)(AsPh_3)_2]$	360	$n \rightarrow \pi^*$
	250	CT
$[CuBr(Htp)(AsPh_3)_2]$	420	CT
	355	$n \rightarrow \pi^*$
	250	CT
$[CuI(Htp)(AsPh_3)_2]$	360	$n \rightarrow \pi^*$
	250	CT
[Ligand(Hcapt)]	365	$n \rightarrow \pi^*$
	280	$\pi \rightarrow \pi^*$
$[CuCl(Hcapt)(PPh_3)_2]$	410	MLCT
	365	$n \rightarrow \pi^*$
$[CuBr(Hcapt)(PPh_3)_2]$	350	$n \rightarrow \pi^*$
	250	CT
$[CuI(Hcapt)(PPh_3)]$	365	$n \rightarrow \pi^*$
	250	CT

...contd.

Table IV.3 (contd.)

Compound	λ_{max} (nm)	Assignments
$[CuCl(Hcapt)(AsPh_3)]$	365	$n \rightarrow \pi^*$
	250	CT
$[CuBr(Hcapt)(AsPh_3)_2]$	360	$n \rightarrow \pi^*$
	250	CT
$[CuI(Hcapt)(AsPh_3)_2]$	365	$n \rightarrow \pi^*$
	250	CT

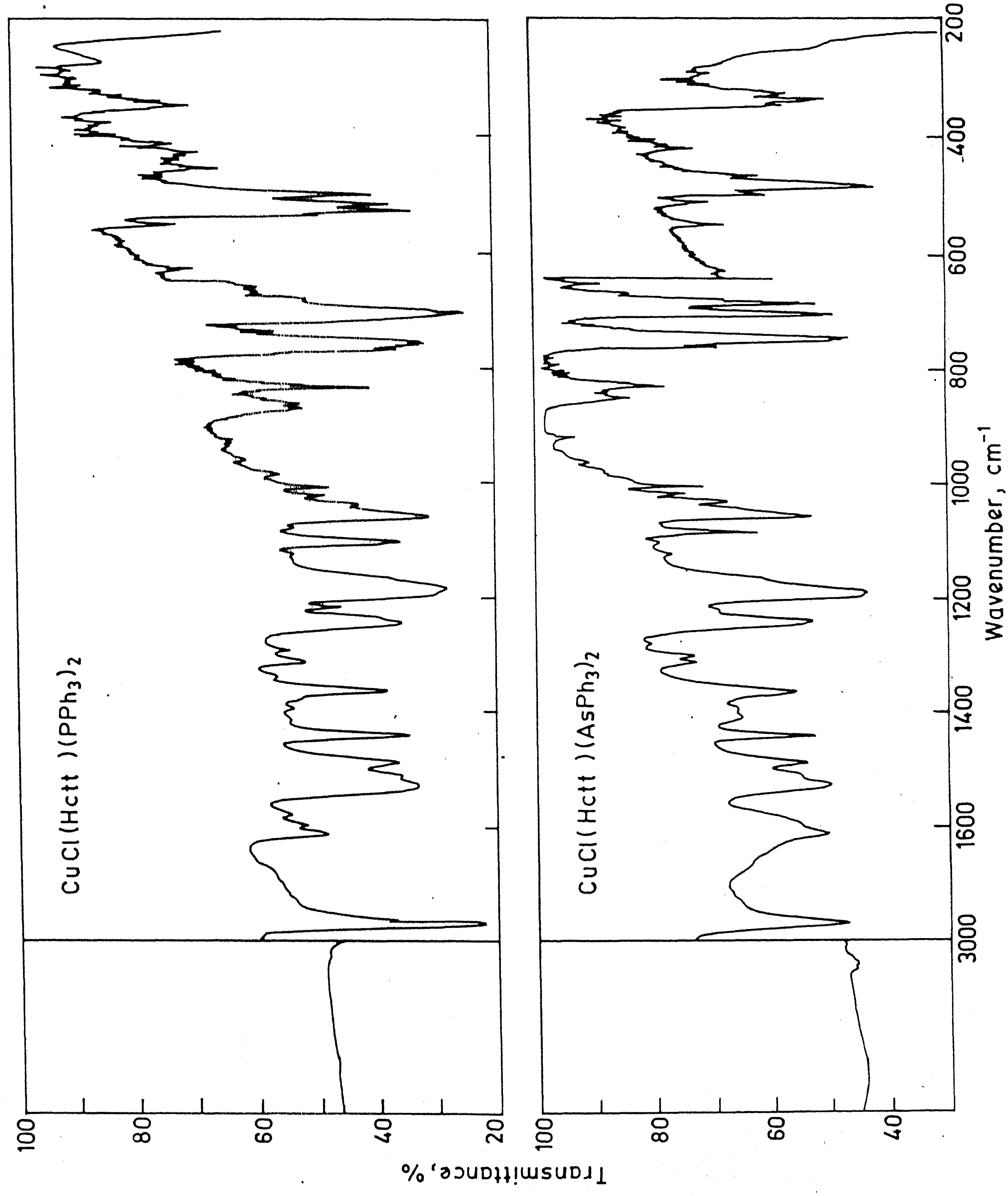
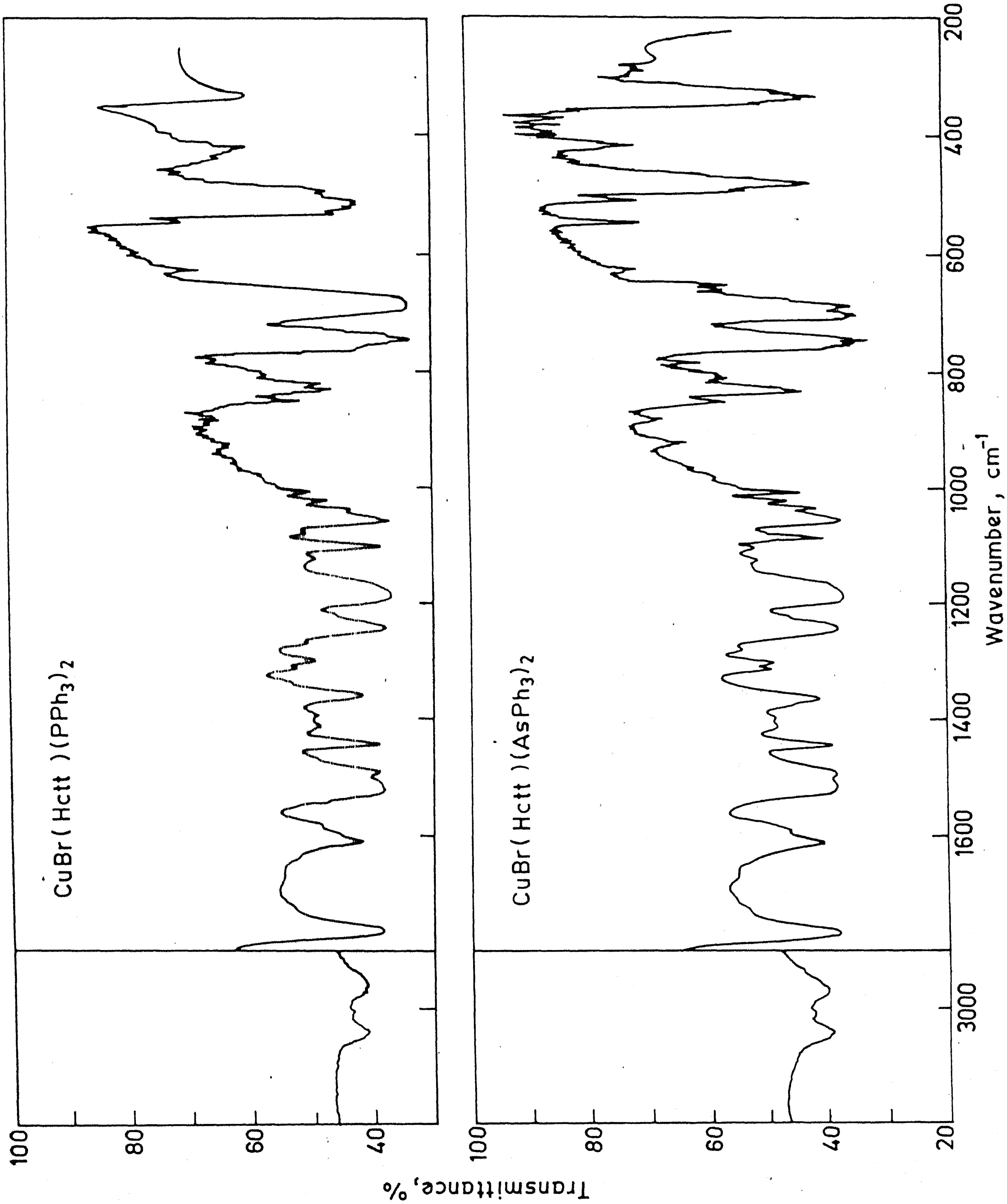
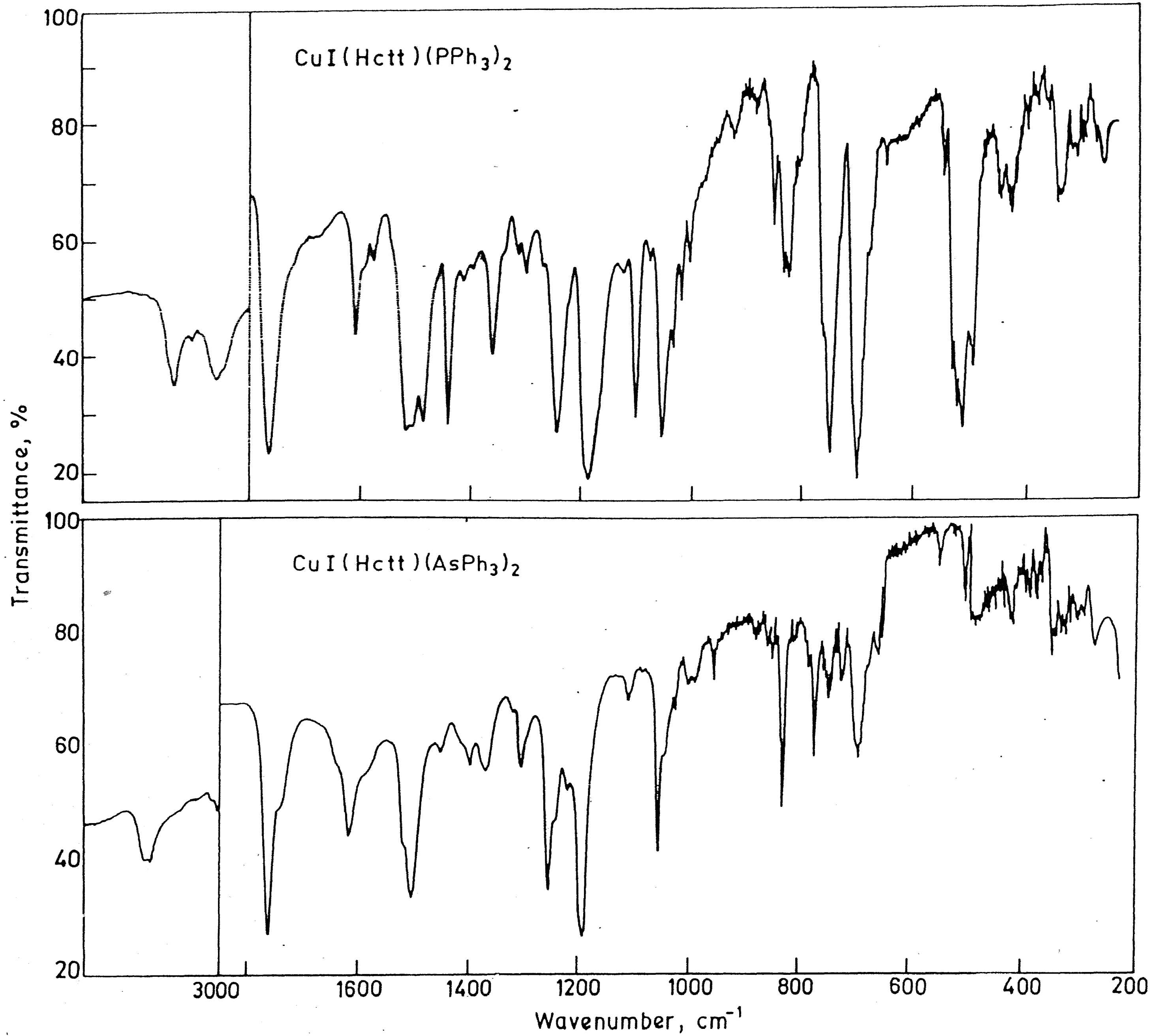

CuCl(Hctt)(PPh$_3$)$_2$
CuCl(Hctt)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
20
3000
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig. IV.1



CuBr(Hctt)(PPh$_3$)$_2$
CuBr(Hctt)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
20
3000
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig. IV.2



CuI(Hctt)(PPh$_3$)$_2$
CuI(Hctt)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
20
Wavenumber, cm^{-1}
3000
1600
1400
1200
1000
800
600
400
200

Fig. IV. 3

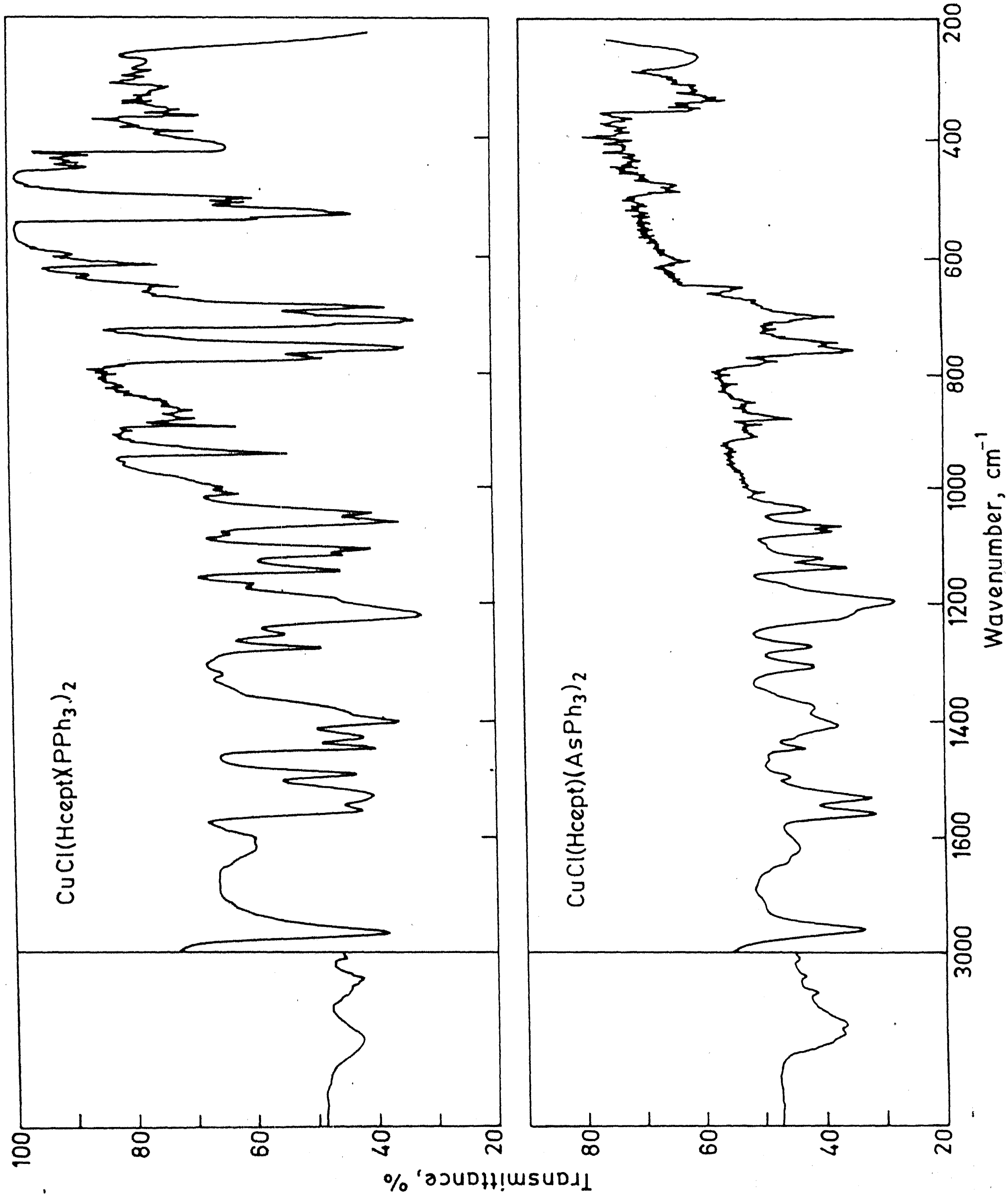

CuCl(Hcept)(PPh$_3$)$_2$
CuCl(Hcept)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
20
Wavenumber, cm^{-1}
3000
1600
1400
1200
1000
800
600
400
200

Fig. IV. 4

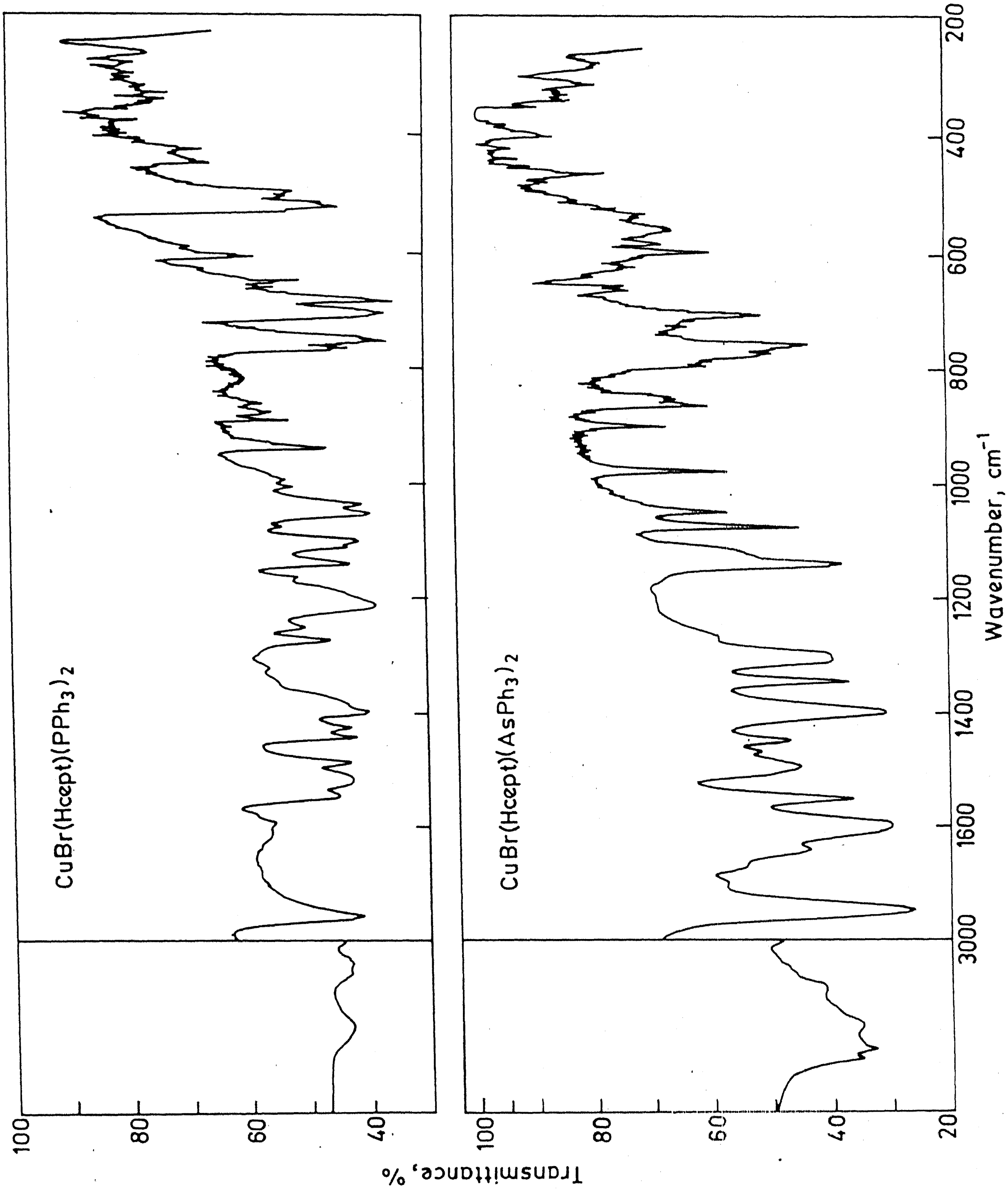

CuBr(Hcept)(PPh$_3$)$_2$
CuBr(Hcept)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
20
3000
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig. IV.5

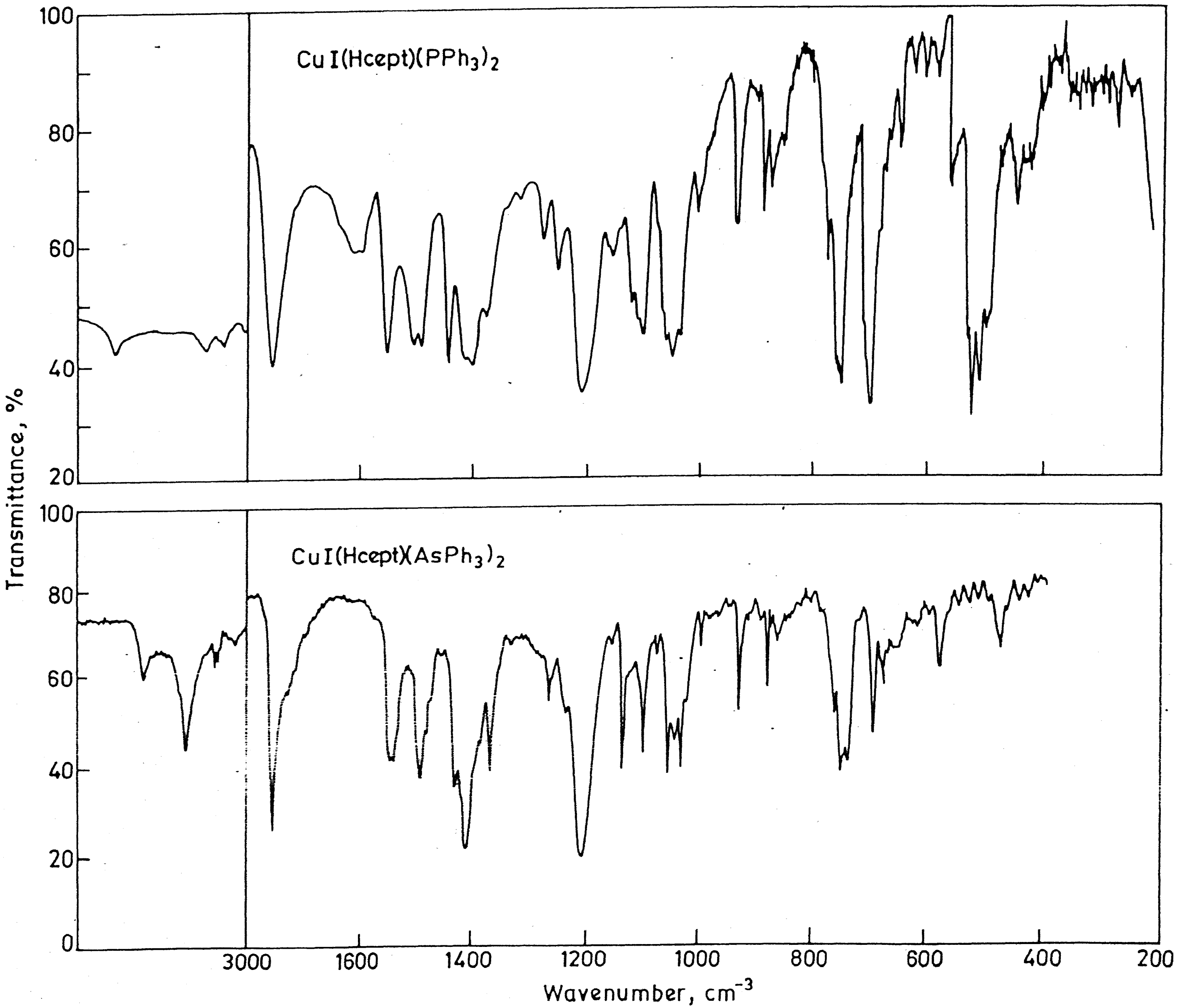

CuI(Hcept)(PPh$_3$)$_2$
CuI(Hcept)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
20
100
80
60
40
20
0
3000
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-3}

Fig. IV. 6

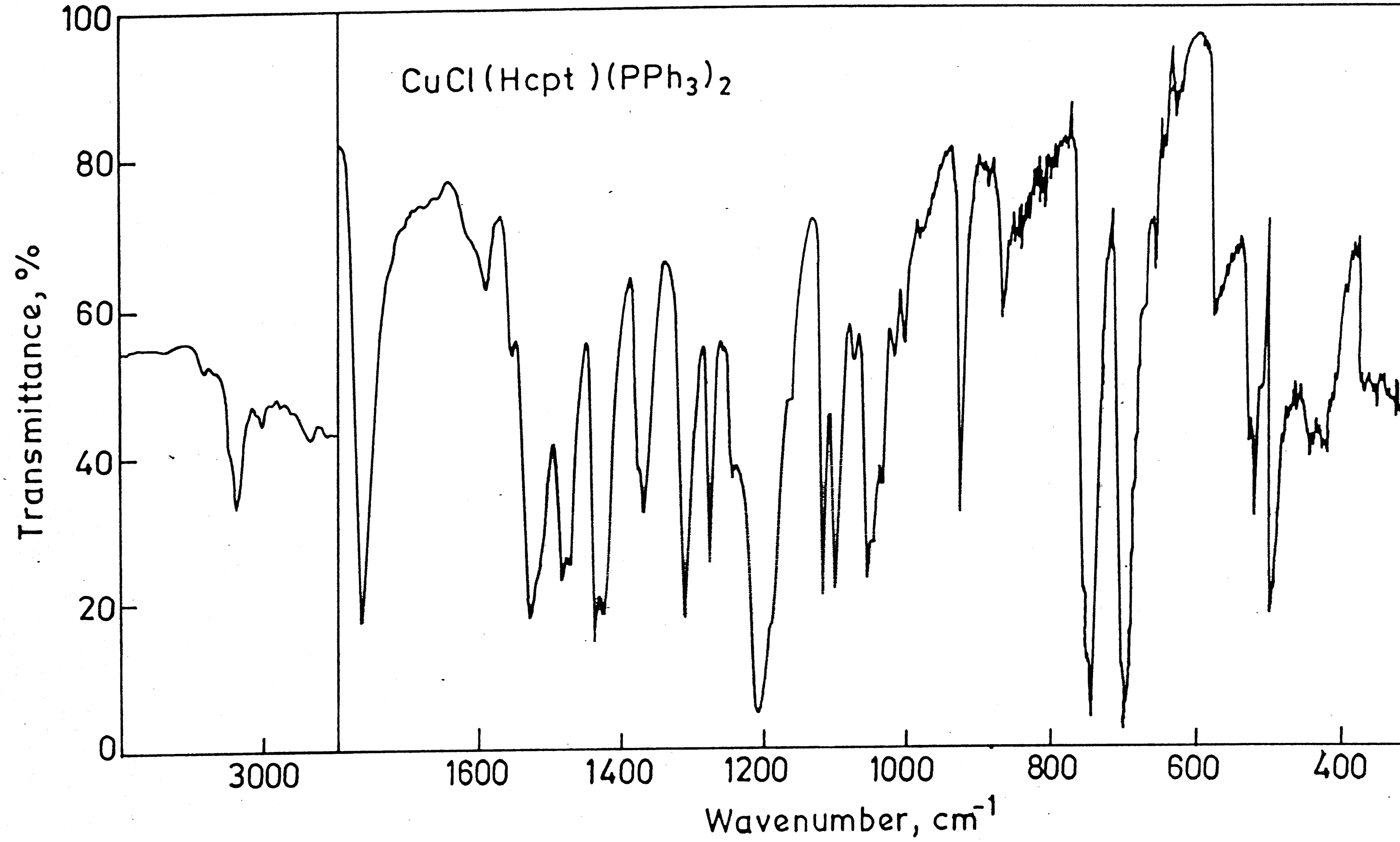

CuCl(Hcpt)(PPh3)2
Transmittance, %
100
80
60
40
20
0
3000
1600
1400
1200
1000
800
600
400
Wavenumber, cm-1

Fig. IV.7

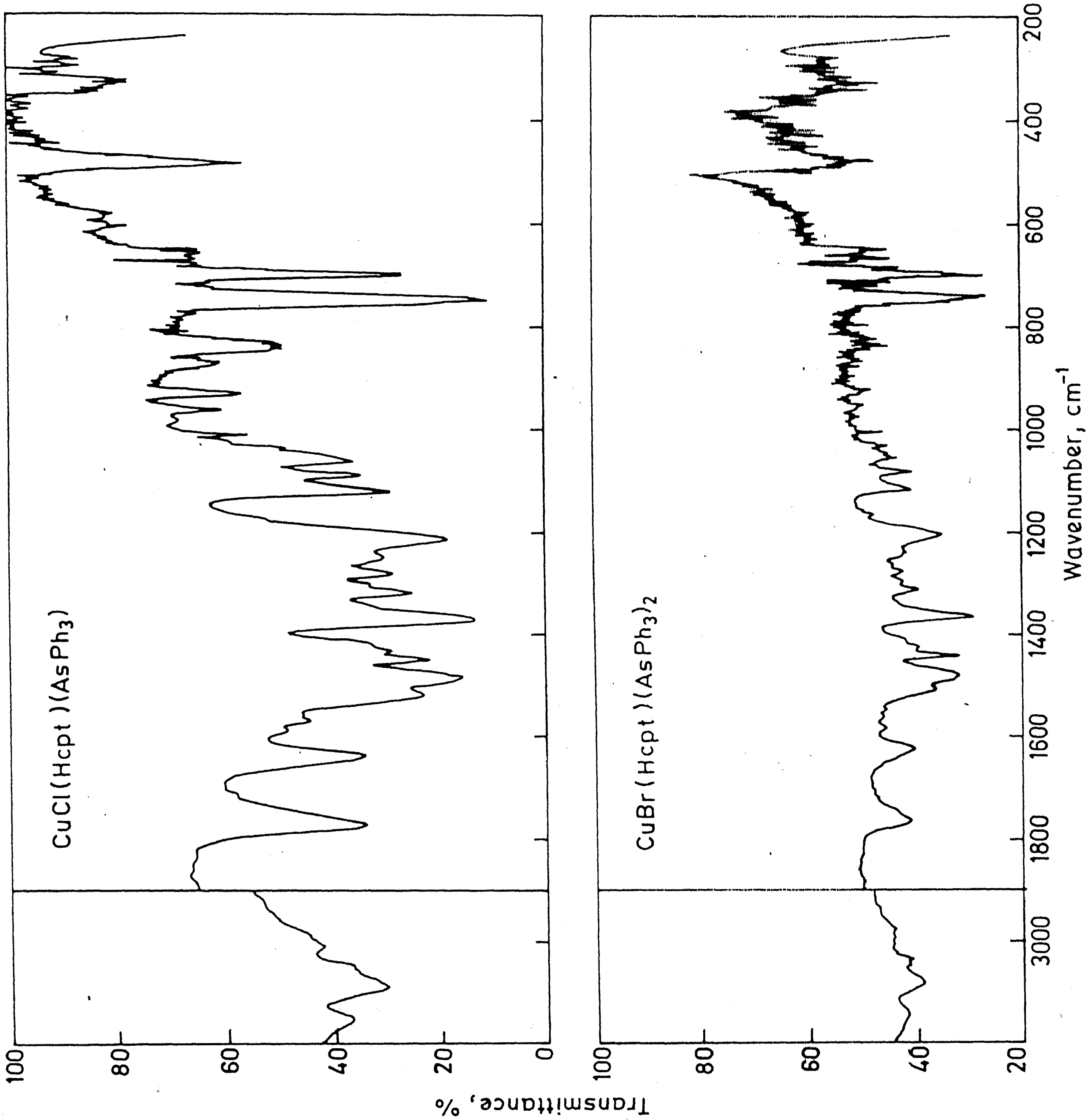

CuCl(Hcpt)(AsPh$_3$)
CuBr(Hcpt)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
20
0
100
80
60
40
20
3000
1800
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig. IV.8

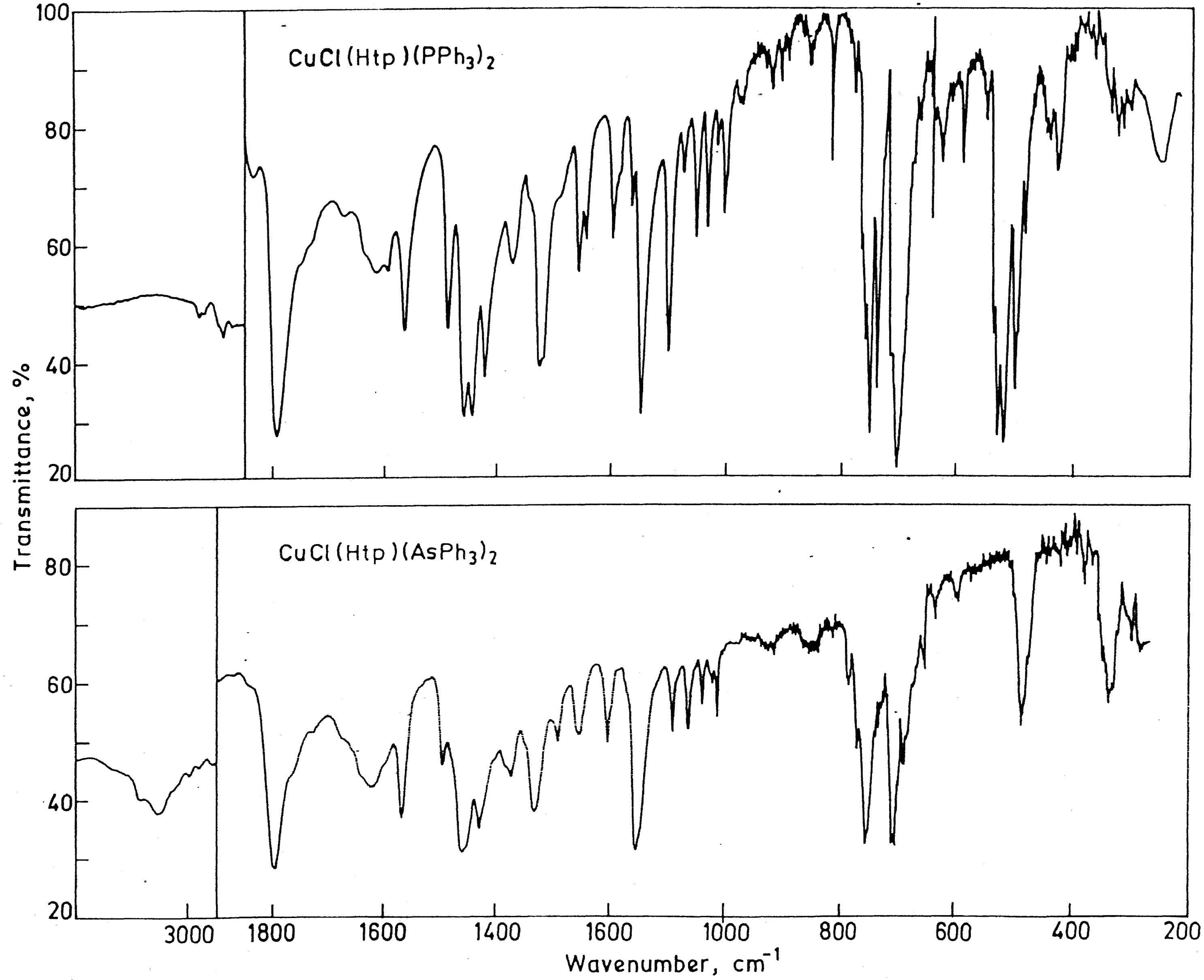

CuCl(Htp)(PPh$_3$)$_2$
CuCl(Htp)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
20
80
60
40
20
3000
1800
1600
1400
1600
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig. IV. 9

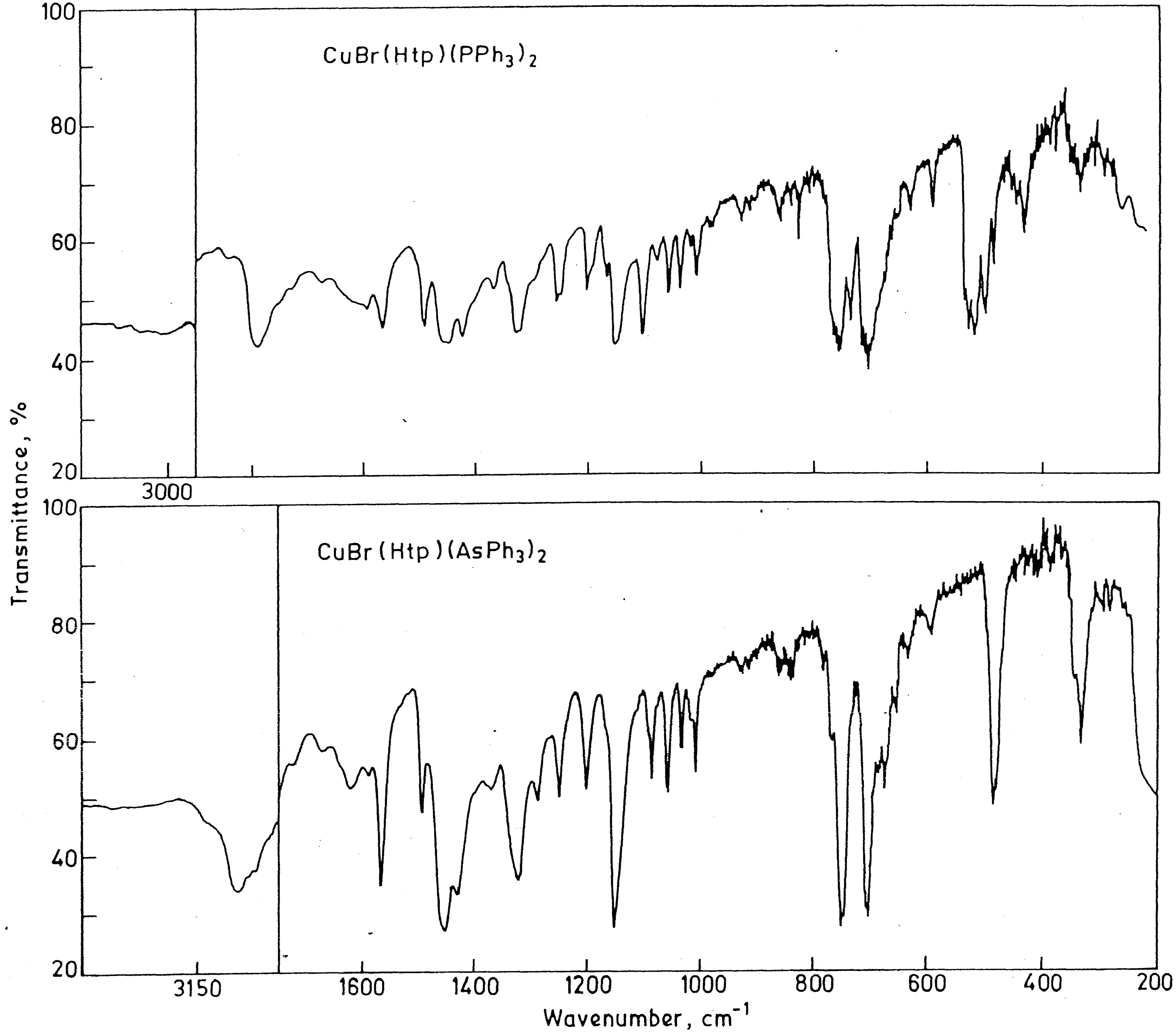

CuBr(Htp)(PPh$_3$)$_2$
CuBr(Htp)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
20
3000
3150
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig. IV.10

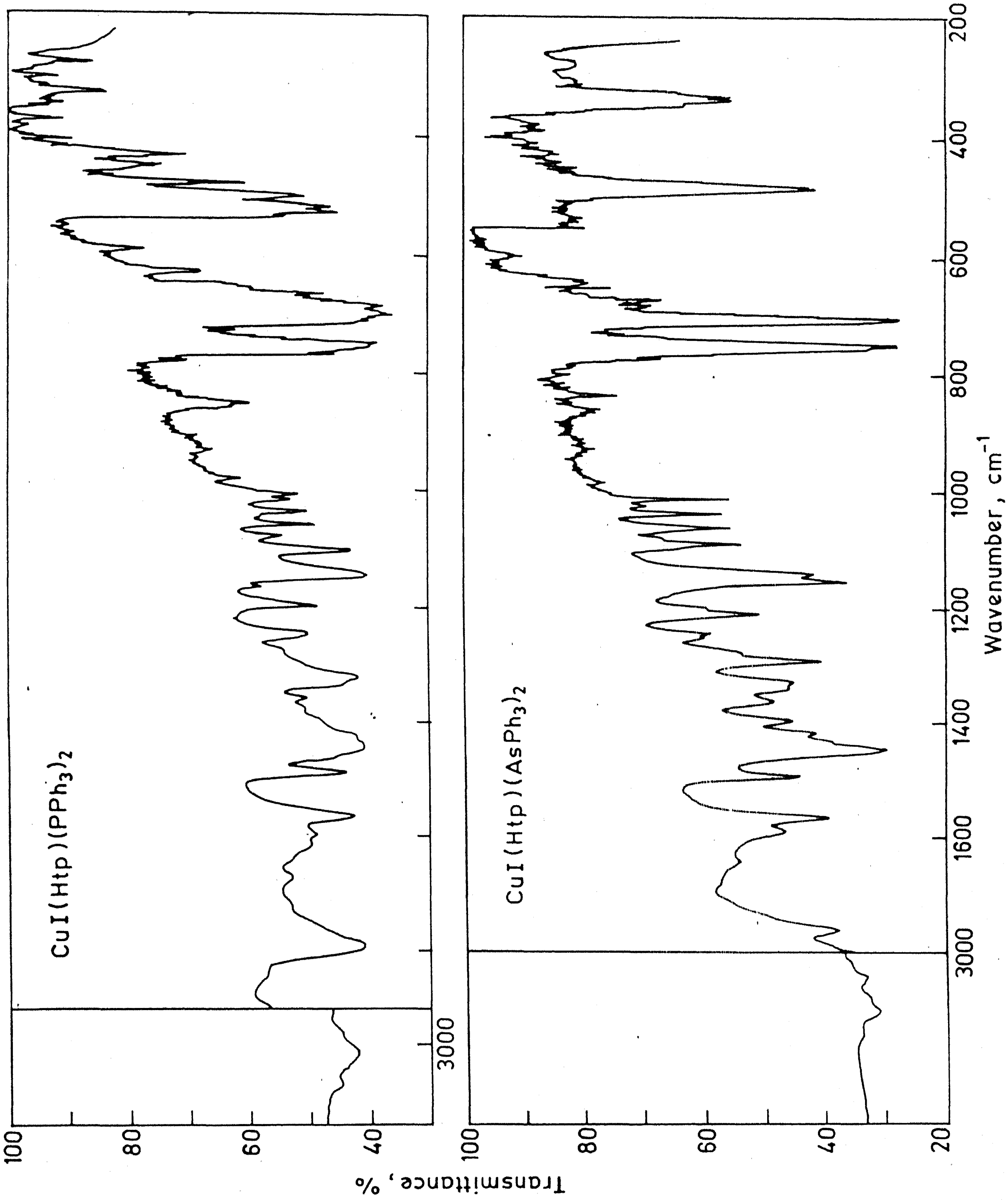
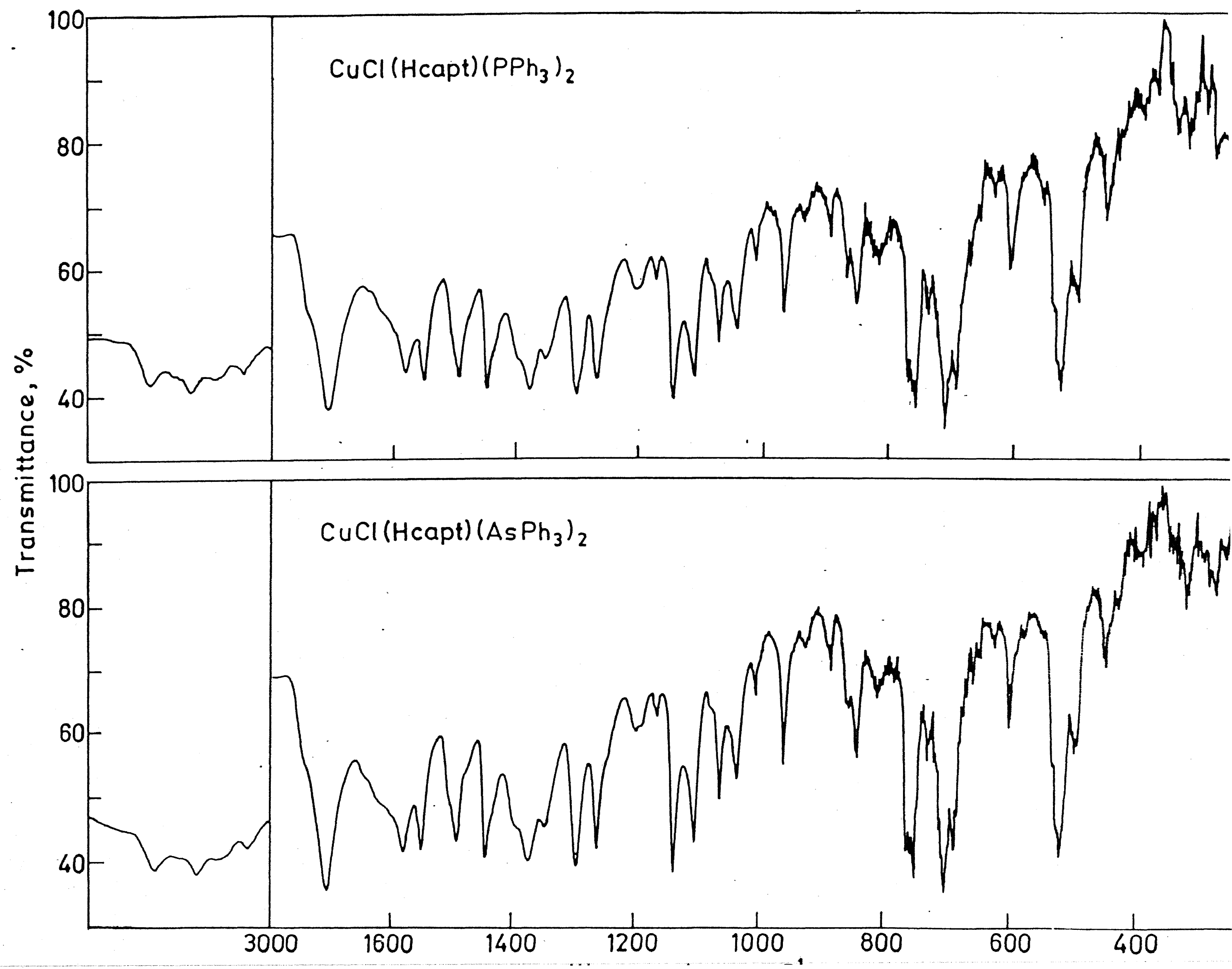
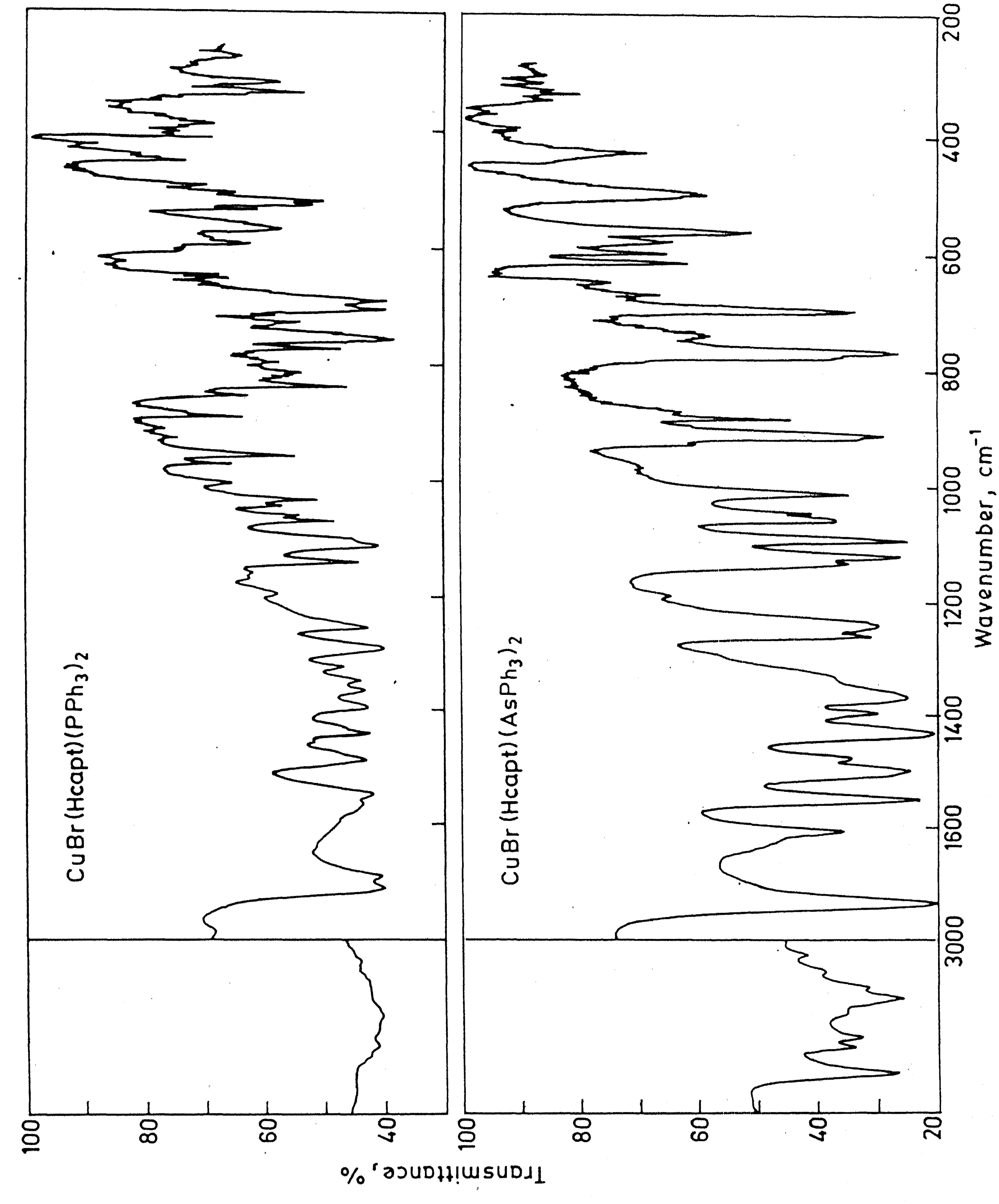

CuI(Htp)(PPh3)2
CuI(Htp)(AsPh3)2
Transmittance, %
100
80
60
40
20
3000
200
400
600
800
1000
1200
1400
1600
Wavenumber, cm-1

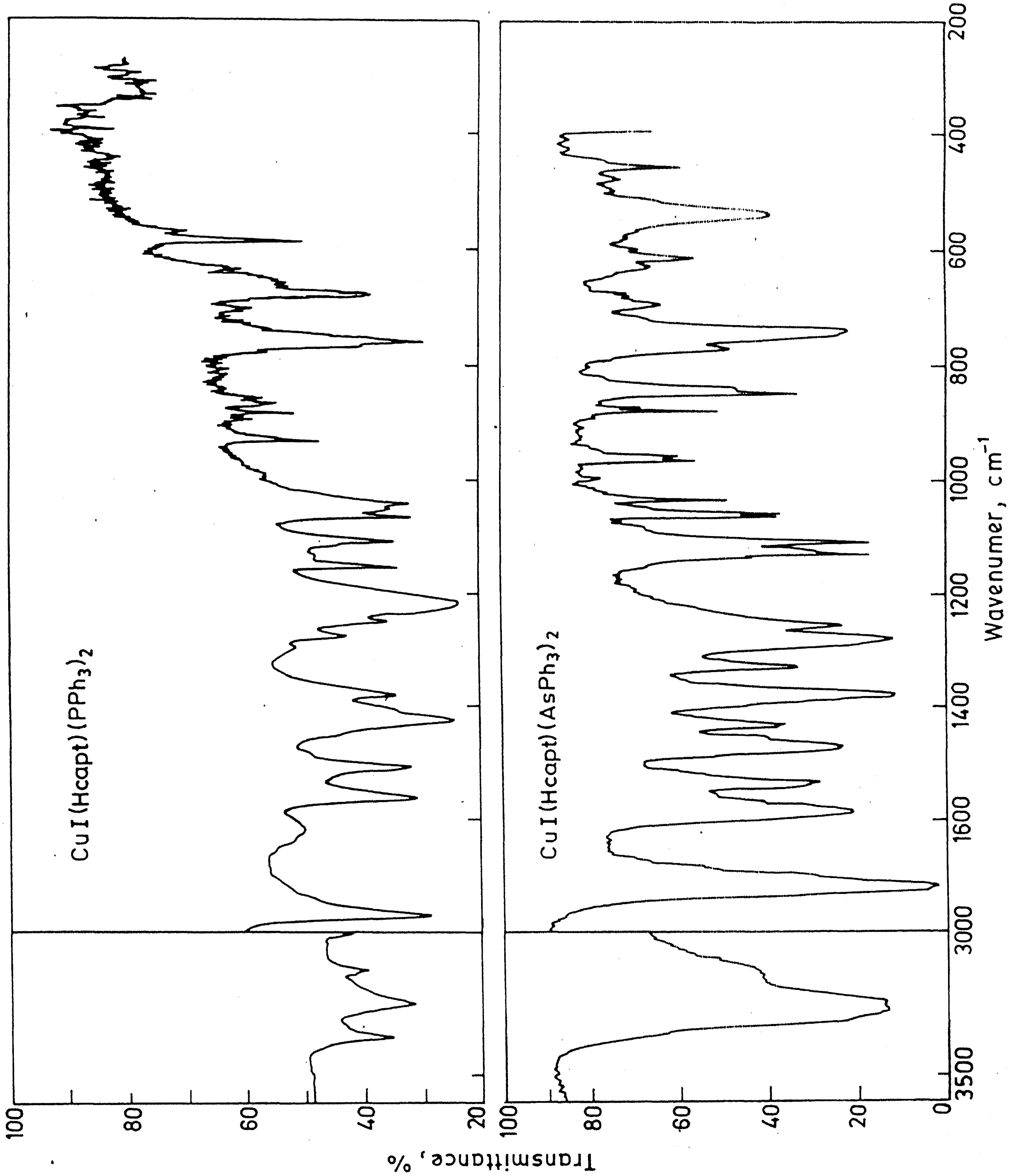
Fig. IV.11


CuCl(Hcapt)(PPh3)2
CuCl(Hcapt)(AsPh3)2
Transmittance, %
100
80
60
40
3000
1600
1400
1200
1000
800
600
400



CuBr(Hcapt)(PPh$_3$)$_2$
CuBr(Hcapt)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
100
80
60
40
20
3000
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig. IV.13



CuI(Hcapt)(PPh$_3$)$_2$
CuI(Hcapt)(AsPh$_3$)$_2$
Transmittance, %
100
80
60
40
20
0
3500
3000
1600
1400
1200
1000
800
600
400
200
Wavenumer, cm^{-1}

Fig. IV.14

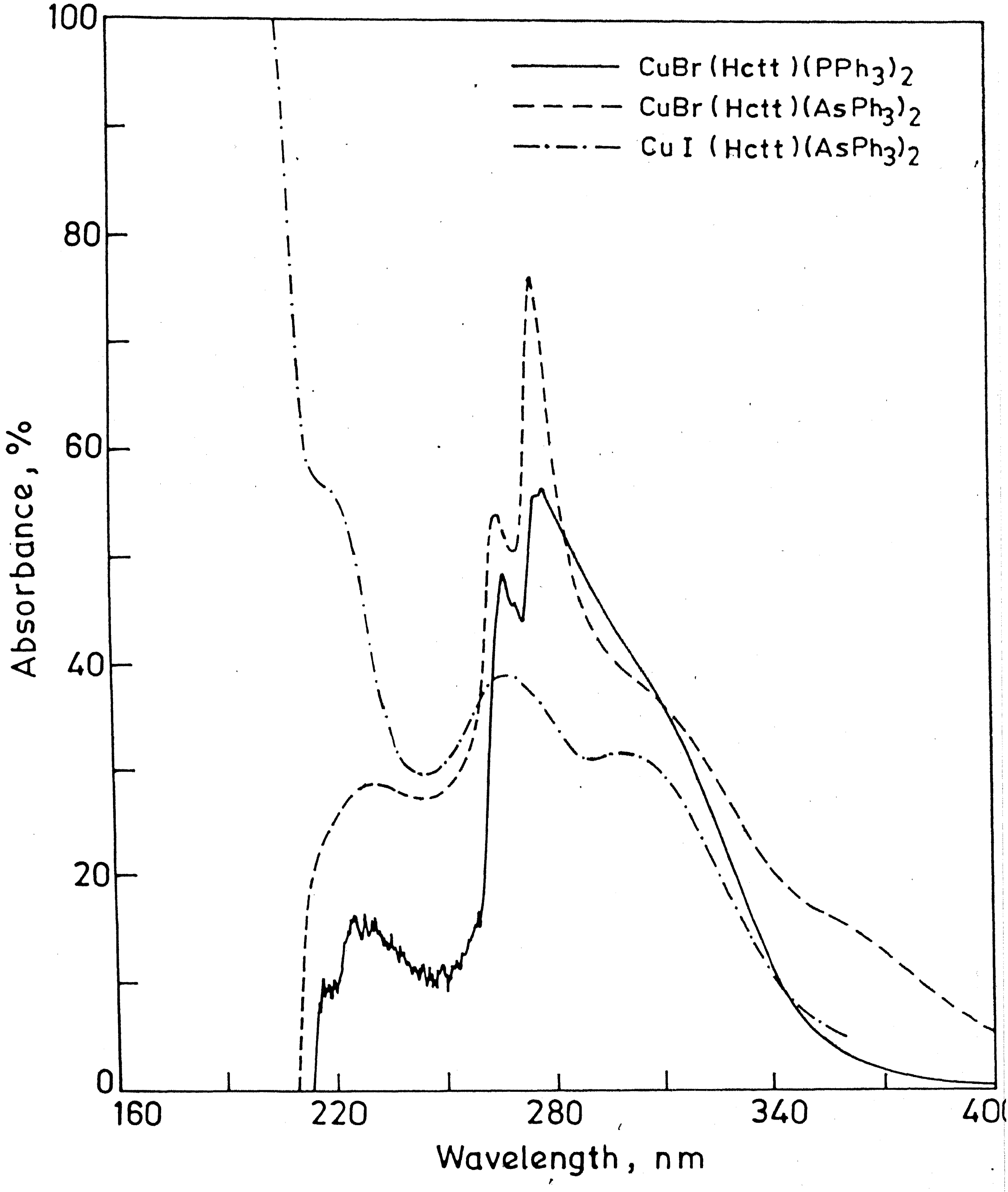

100
80
60
40
20
0
Absorbance, %
160
220
280
340
400
Wavelength, nm
CuBr (Hctt)(PPh3)2
CuBr (Hctt)(AsPh3)2
Cu I (Hctt)(AsPh3)2

Fig. IV.15

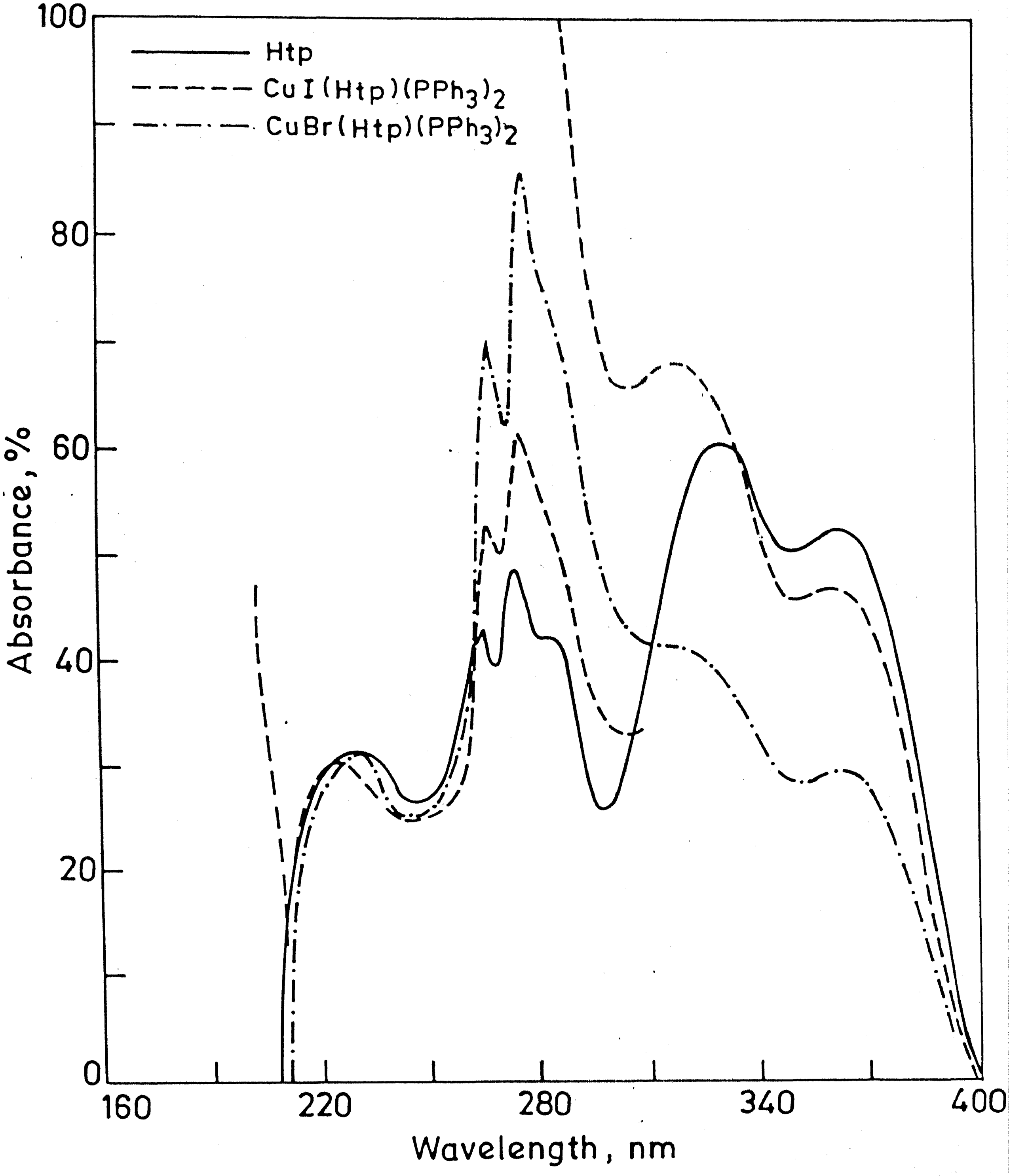

Htp
CuI(Htp)(PPh3)2
CuBr(Htp)(PPh3)2
100
80
60
40
20
0
Absorbance, %
160
220
280
340
400
Wavelength, nm

Fig. IV.16

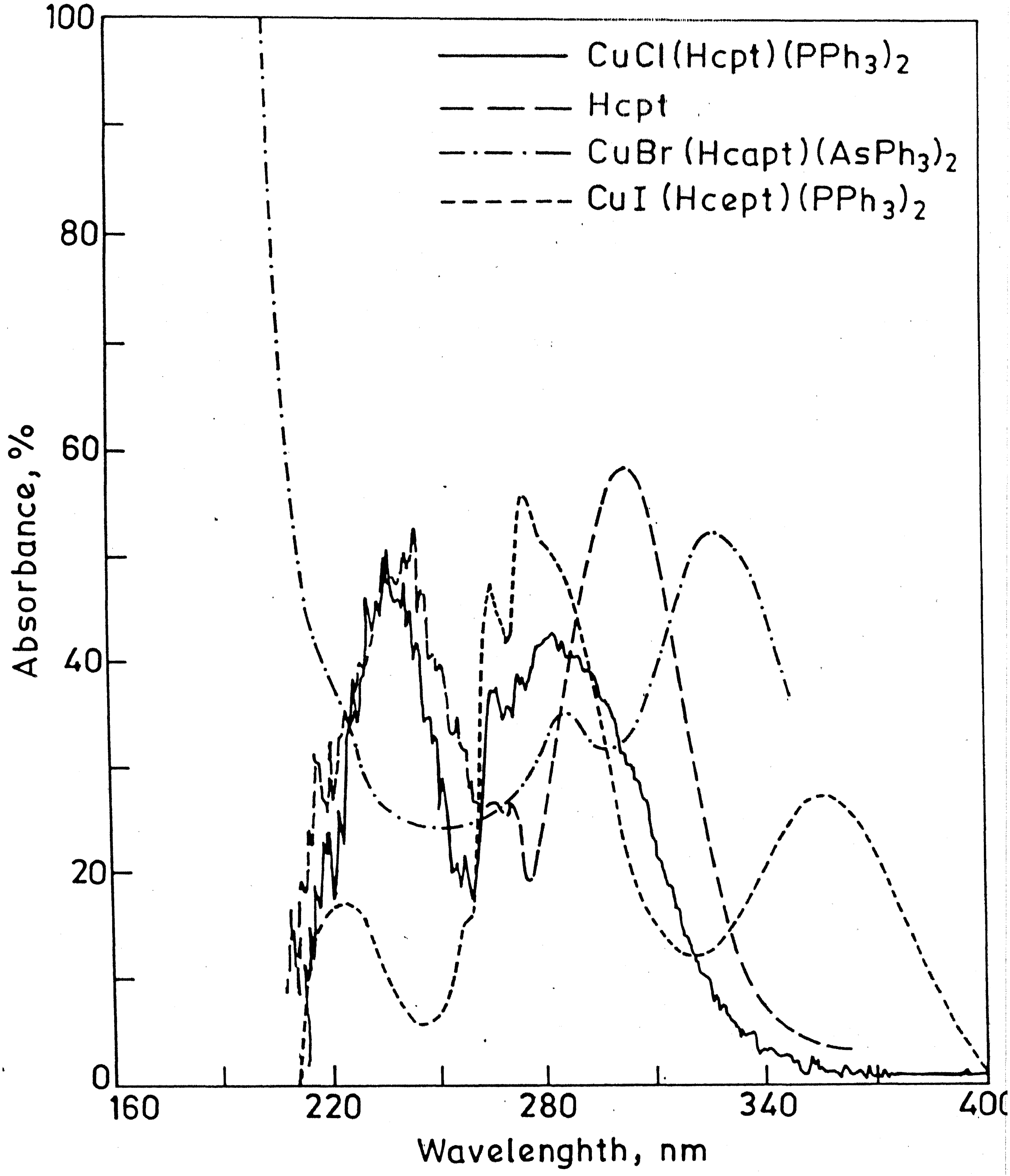

CuCl(Hcpt)(PPh3)2
Hcpt
CuBr (Hcapt)(AsPh3)2
CuI (Hcept)(PPh3)2
100
80
60
40
20
0
Absorbance, %
160
220
280
340
400
Wavelenghth, nm

Fig. IV. 17

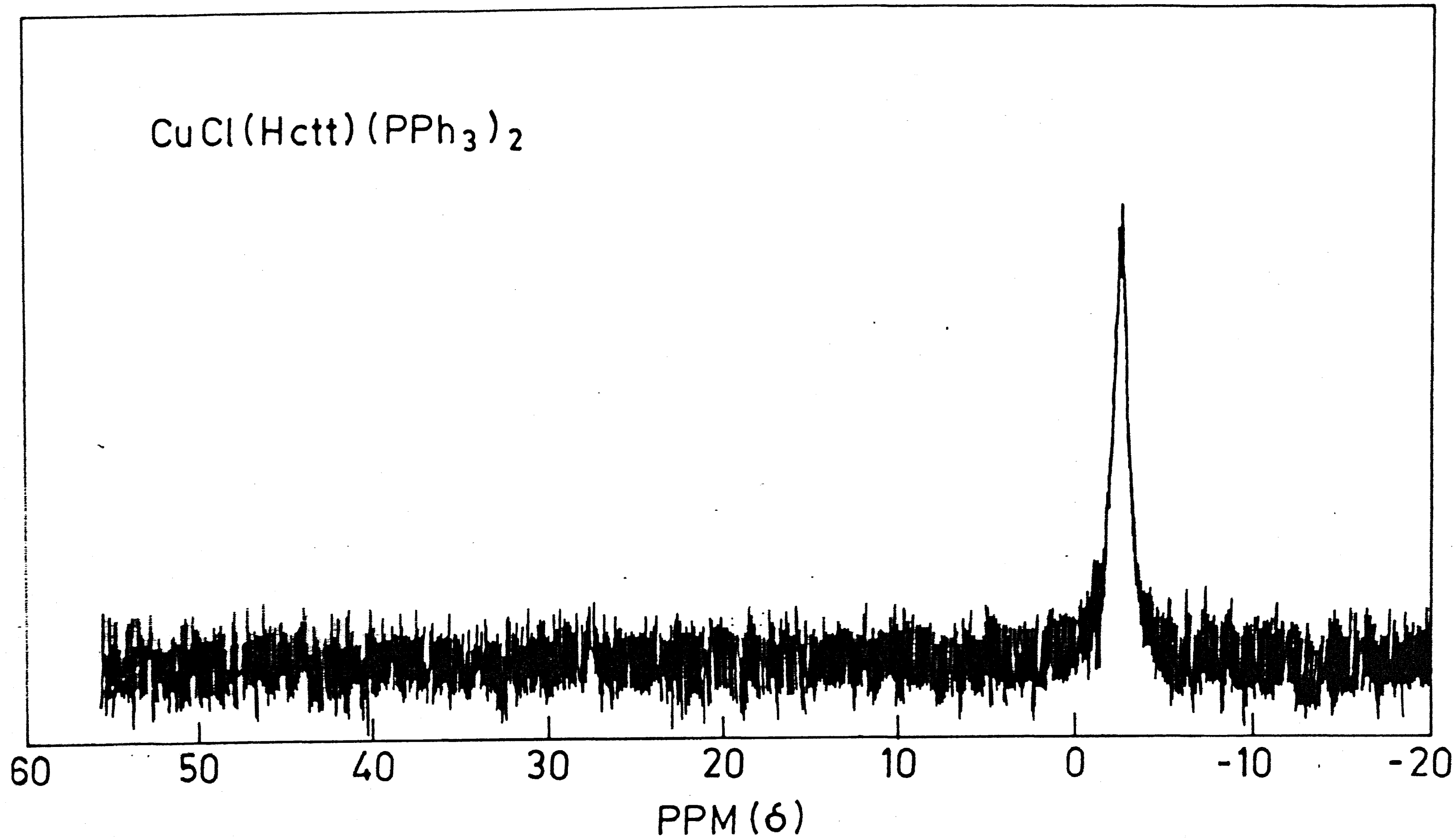


Fig. IV.18

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CHAPTER V

INVESTIGATION OF THE REACTIONS OF AROMATIC THIOAMIDES, 2-THIOPYRROLE-1,2-DICARBOXIMIDE AND 2-THIONE-3-PHENYL-4-QUINAZOLINONE WITH $[RuCl_2(CO)_2]$, $[RuCl_2(PPh_3)_3]$ AND $[(\eta^5-C_5H_5)RuCl(AsPh_3)_2]$: A NOVEL SERIES OF RUTHENIUM(II) COMPLEXES WITH LIGANDS CONTAINING H-N-C=S GROUP

This chapter describes the reactions of $[RuCl_2(CO)_2]$, $[RuCl_2(PPh_3)_3]$ and $[(\eta^5-C_5H_5)RuCl(AsPh_3)_2]$ with aromatic thioamides ArCSNHCOR (Ar = 1-pyrrolyl, 2-pyrrolyl, 4-tolyl, 2-thienyl; R = OC_2H_5, NH_2, NHPh), 2-thiopyrrole-1,2-dicarboximide and 2-thione-3-phenyl-4-quinazolinone. $RuCl_2(PPh_3)_3$ gives $RuCl_2$-(ligand)$_2$(PPh_3).XCH_2Cl_2 (X = 0, 1/2 or 1). Oxidation state of ruthenium was established with the help of magnetic susceptibility and e.s.r. studies. These reactions were carried out in dry N_2 atmosphere. Similarly the reactions of the ligands with $[(\eta^5-C_5H_5)RuCl(AsPh_3)_2]$ and $[RuCl_2(CO)_2]$ led to the formation of the diamagnetic compounds of the type $[(\eta^5-C_5H_5)RuCl(\text{ligand})(AsPh_3).XCH_2Cl_2]$ (X = 0 or 1/2) and $[RuCl_2(CO)_2(\text{ligand})]$ respectively. The presence of dichloromethane in the compounds was confirmed with the help of ^1H nmr spectral studies apart from chemical analyses. The coordination modes of the ligands were

established on the basis of i.r. and ^{1}H n.m.r. spectral data. All the Ru(II) diamagnetic complexes have been assigned distorted/quasi-octahedral geometry.

V.1 EXPERIMENTAL

All the chemicals used were either of Analar or chemically pure grade. Solvents were dried before use and all the reactions were carried out under dry N_2 atmosphere. The methods of elemental analyses, recording of I.R. spectra, melting points and magnetic measurements have been described in previous chapters. The electronic spectra were recorded on Shimadzu double beam spectrophotometer UV-190. The proton N.M.R. spectra were recorded on a Varian's EM-390 90 MHz spectrometer in the range δ 0-20 ppm in $CDCl_3$ using tetramethylsilane (TMS, $\delta = 0$) as calibrant. The conductivity measurements of the complexes were made on a Elico conductivity meter type CM-80. Starting compounds $[RuCl_2(CO)_2]$,[1] $[RuCl_2(PPh_3)_3]$[2] and $[(\eta^5-C_5H_5)RuCl(AsPh_3)_2]$[3] were prepared by literature methods.

V.1.1 Preparation of Complexes

(i) Preparation of the complexes $[RuCl_2(CO)_2(ligand)]$

(ligand = Hctt, Hcept, Hcpt, Hcett, Hcapt, Hcppt, Htp or Htpq)

50 ml of methanol solution containing 0.114 g of $[RuCl_2-(CO)_2]$ (0.5 mmol) and 0.5 mmol of appropriate ligand was refluxed

for 5-6 hrs. The resulting solution was concentrated upto almost dryness under reduced pressure, the residue was dissolved in minimum quantity of CH_2Cl_2, followed by an addition of excess (150 ml) petroleum ether with constant stirring. On standing for 1-2 hrs, the precipitate settled down. It was centrifuged, washed several times with petroleum ether and dried *in vacuo*.

(ii) **Preparation of complexes $[RuCl_2(ligand)_2(PPh_3).XCH_2Cl_2$**

(X = 0, 1/2 or 1; ligand = Hctt, Hcept, Hcpt, Hcett, Hcapt, Hcppt, Htp or Htpq).

50 ml of CH_2Cl_2 solution containing 0.100 g of $[RuCl_2(PPh_3)_3$. (0.1 mmol) and 0.1 mmol of appropriate ligand was refluxed under dry N_2 for 3 hrs. The resulting solution was concentrated upto almost dryness under reduced pressure, the residue was dissolved in minimum quantity of dichloromethane, followed by an addition of petroleum ether with constant stirring. On standing for 1-2 hrs the precipitate settled down. It was centrifuged, washed several times with petroleum ether and dried in vacuo.

(iii) **Preparation of the complexes $[(\eta^5-C_5H_5)RuCl(ligand)(AsPh_3)$- 1/2 $CH_2Cl_2]$**

(ligand = Hctt, Hcept, Hcpt, Hcett, Hcapt*, Hcppt*, Htp or Htpq

In about 40 ml of methanol solution containing $[(\eta^5-C_5H_5)$-$RuCl(AsPh_3)_2]$ (0.105 g, 0.25 mmol), 25 ml methanol solution of appropriate ligand (0.35 mmol) was added under dry N_2. The

resulting mixture was stirred for 2-3 hrs. (In case of Hcapt and Hceppt compound was separated during stirring.) The resulting solution was concentrated upto dryness under reduced pressure, the residue was dissolved in minimum quantity of CH_2Cl_2 followed by addition of petroleum ether. On scratching the walls of beaker and allowing to stand for 1-2 hrs, the precipitate appears. It was centrifuged, washed several times with petroleum ether and dried _in vacuo_.

*In case of these ligands (Hcapt and Hcppt) orange complexes of the formula $(\eta^5-C_5H_5)RuCl(AsPh_3)$(ligand) were precipitated during stirring which were isolated by centrifugation and washed with petroleum ether. The filtrate was concentrated upto dryness under reduced pressure. The residue was dissolved in minimum quantity of dichloromethane followed by addition of petroleum-ether. On scratching the walls of the beaker and allowing to stand for 1-2 hrs, the precipitate $[(\eta^5-C_5H_5)RuCl(AsPh_3)(\text{ligand})]$-1/2 CH_2Cl_2 appears, which was centrifuged, washed several times with petroleum ether and dried _in vacuo_.

V.1.2 Estimation of Phosphorus[4]

Samples were decomposed with a fusing mixture (Na_2O_2, sugar and $NaNO_3$ in the ratio 20:1:3 in a parr-bomb). The melt was extracted with water and heated to SO_3 fumes after adding concentrated H_2SO_4. It was diluted with water and filtered if necessary. In the filtrate phosphorus was estimated as ammonium-phosphomolybdate.

V.2 RESULTS AND DISCUSSION

Analytical data are consistent with the stoichiometry proposed for the complexes (Table V.1). Conductivity measurements show that they are nonionic in nature. The compounds are, in general, air stable and soluble in most of the organic solvents. All the complexes were found diamagnetic, indicating +2 oxidation state of ruthenium. Diamagnetic nature of the complexes was also confirmed by X-band e.s.r. studies, as no signal appeared at room temperature.

V.2.1 $[RuCl_2(CO)_2(ligand)]$ (ligand = Hctt, Hcept, Hcpt, Hcett, Hcapt, Hcppt, Htp or Htpq)

V.2.1.1 IR and ^1H NMR Spectra

The mode of bonding of ligands were decided on the basis of shifts (Table V.2) in the positions of ν(NH), ν(C=O), ν(C=S) and four thioamide bands after complexation.

(i) $RuCl_2(CO)_2(Hctt)$

Band at 1765 cm^{-1} ($\nu_{C=O}$) shifts to 1770 cm^{-1} excluding the possibility of carbonyl oxygen as donor site. Bands at 1130 cm^{-1} ($\nu_{C=S}$) and 850 cm^{-1} (thioamide band IV) in the i.r. spectrum of the ligand appear at 1115 and 840 cm^{-1} in the complex with reduced intensity. This observation supports the bonding through thiocarbonyl sulfur. The band at 1540 cm^{-1} (thioamide band I) shifts to lower wave number (1500 cm^{-1}) indicating metal nitrogen bond

formation. Thioamide band I[5] ($\delta_{N-H} + \nu_{C \cdots N}$) will undergo red shift in case of bonding through nitrogen whereas it will show blue shift because of bonding through sulfur. Final decrease in the position of 1540 cm^{-1} band indicates relatively stronger interaction of nitrogen with metal. Thioamide band II ($\nu_{C \cdots N}$ + $\delta_{NH} + \delta_{CH}$) (1360 cm^{-1}) and thioamide band III ($\nu_{C=S} + \nu_{C-N}$)[6] (1075 cm^{-1}) as expected shift to lower wave numbers 1320 and 1040 cm^{-1}, respectively.

(ii) $RuCl_2(CO)_2(Hcept)$

(a) Band at 1765 cm^{-1} ($\nu_{C=O}$) shifts to 1745 cm^{-1}.

(b) Thioamide band I at 1540 cm^{-1} shifts to 1555 cm^{-1}.

(c) Thioamide band II at 1340 cm^{-1} also shifts to higher wave number 1385 cm^{-1}.

(d) Band at 1120 cm^{-1} ($\nu_{C=S}$) appears at 1100 cm^{-1}.

(e) Thioamide band III at 1070 cm^{-1} remains constant.

(f) Thioamide band IV at 870 cm^{-1} goes to lower wave number 865 cm^{-1}.

The above account of infrared spectral changes indicate that the Hcept is chelating through S and O atoms.

(iii) $RuCl_2(CO)_2(Hcpt)$

A band at 3210 cm^{-1} (ν_{NH}) present in the ligand goes down by (-30 cm^{-1}) which can be tentatively thought of Ru(II)-nitrogen bond formation. The band at 1730 cm^{-1} ($\nu_{C=O}$) shifts to 1790 cm^{-1}

excluding the possibility of carbonyl oxygen as donor site. Bands at 1125 cm^{-1} ($\nu_{C=S}$) and 880 cm^{-1} (thioamide band IV) appear at 1115 cm^{-1} and 860 cm^{-1} in the complex, supporting bonding through thiocarbonyl sulfur. Thioamide band I ($\nu_{C\cdots N} + \delta_{NH}$) present at 1500 cm^{-1} in the spectrum of the ligand undergoes red shift (1480 cm^{-1}). The ligand is thus NS donor. Thioamide band II ($\nu_{C\cdots N} + \delta_{NH} + \delta_{CH}$) (1320 cm^{-1}) and thioamide band III ($\nu_{C=S} + \nu_{C\cdots N}$) (1015 cm^{-1}) as expected, shift to lower wave numbers.

iv) $RuCl_2(CO)_2$(Hcett)

The following changes are observed in the i.r. spectrum of the ligand after reaction with $RuCl_2(CO)_2$:

(a) A band at 3240 cm^{-1} (ν_{NH}) becomes broad.

(b) Band at 1730 cm^{-1} goes up by 20 cm^{-1}.

(c) Thioamide band I at 1510 cm^{-1} shifts to 1500 cm^{-1}.

(d) Thioamide bands II and III at 1360 and 1020 cm^{-1} shift to lower wave numbers 1345 and 1000 cm^{-1}, respectively.

(e) Thioamide band IV at 770 cm^{-1} undergoes red shift by 50 cm^{-1}.

Above spectral shifts unequivocally establish that the ligand is NS donor.

(v) $RuCl_2(CO)_2$(Hcapt)

The following i.r. shifts are observed after Hcapt reacts with $RuCl_2(CO)_2$ to give the product:

(a) A band at 1730 cm^{-1} ($\nu_{C=O}$) shifts to 1690 cm^{-1}.

(b) Bands at 1120 cm^{-1} ($\nu_{C=S}$) and 845 cm^{-1} (thioamide band IV shift to higher wave numbers 1130 and 860 cm^{-1}, respectively.

(c) A band at 1580 cm^{-1} ($\nu_{C=N}$) goes down giving a sharp peak at 1550 cm^{-1}.

(d) Thioamide band II at 1330 cm^{-1} goes to lower wave number 1310 cm^{-1} whereas thioamide band III at 1060 cm^{-1} goes to 1070 cm^{-1}.

The above observations establish almost definitely that Hcapt is NO donor.

(vi) <u>$RuCl_2(CO)_2$(Hcppt)</u>

Band at 1720 cm^{-1} ($\nu_{C=O}$) shifts to 1680 cm^{-1}, whereas thioamide band I ($\nu_{C\equiv N} + \delta_{NH}$) at 1520 cm^{-1} undergoes red shift by 10 cm^{-1}. Bands at 1125 cm^{-1} ($\nu_{C=S}$) and 860 cm^{-1} (thioamide band IV) shift to higher wave numbers 1140 and 870 cm^{-1}, respectively. The above shifts in the i.r. bands of Hcppt after complexation indicate that the ligand is NO donor and thiocarbonyl sulfur is excluded as donor site. The net lowering of 1520 cm^{-1} band indicates relatively stronger interaction of Ru(II) ion with nitrogen as compared to sulfur. Thioamide band I and II at 1350 and 1000 cm^{-1} shift to 1320 and 1010 cm^{-1}, respectively.

(vii) <u>$RuCl_2(CO)_2$(Htp)</u>

The band at 1765 cm^{-1} ($\nu_{C=O}$) shifts to higher wave number

indicating non-involvement of carbonyl oxygen in the Ru(II)-oxygen bond formation. The bands at 1140 cm^{-1} ($\nu_{C=S}$) and thioamide band IV (850 cm^{-1}) shift to lower wave numbers (1135 cm^{-1} and 810 cm^{-1}) indicating the bonding through thiocarbonyl sulfur. Thioamide band I (δ_{NH} + $\nu_{C \cdots N}$) at 1555 cm^{-1} present in the ligand goes down by 15 cm^{-1} (1540 cm^{-1}). This observation indicates that the ligand Htp is bidentate through N & S atoms. ν_{NH} is affected by various factors after complexation, hence cannot be used for identifying donor site with reliability. Thioamide band II ($\nu_{C \cdots N}$ + δ_{NH} + δ_{CH}) at 1305 cm^{-1} disappears and thioamide band III ($\nu_{C=S}$ + ν_{C-N}) as expected shifts to lower wave numbers.

(viii) $\underline{RuCl_2(CO)_2(Htpq)}$

(a) A band at 3250 cm^{-1} (ν_{NH}) becomes broad.

(b) Band at 1660 cm^{-1} ($\nu_{C=O}$) goes up by 20 cm^{-1}.

(c) Thioamide band I at 1540 cm^{-1} shifts to 1530 cm^{-1}.

(d) Thioamide bands II and III at 1345 and 1000 cm^{-1} shift to lower wave numbers 1330 and 980 cm^{-1}, respectively.

(e) Thioamide band IV at 770 cm^{-1} undergoes red shift by 20 cm^{-1}.

Above spectral shifts unequivocally establish that the ligand is NS donor.

Two C≡O stretching frequencies in the parent compound are at 2060 and 2000 cm^{-1}. In all the cases, both the C≡O stretching bands shift to higher frequencies (maximum 80 cm^{-1}). This

observation establishes that the title ligands are weak π-acid ligands. The medium intensity bands present in the region 330-450 cm^{-1} may be due to coupled vibrations of terminal ν(Ru-Cl), ν(Ru-S) and ν(Ru-N).[7]

The NH proton resonance in case of complex with Hctt was observed at δ11.3 ppm whereas it could not be observed for other complexes. The n.m.r. spectra of the complexes showed the proton resonance of dichloromethane at δ5.3-5.4 and all the characteristic signals of concerned ligands (Table V.3).

V.2.2 [$RuCl_2$(ligand)$_2$(PPh_3).XCH_2Cl_2 (X = 0, 1/2 or 1) (ligand = Hctt, Hcept, Hcpt, Hcett, Hcapt, Hcppt, Htp or Htpq)

V.2.2.1 IR and ^{1}H NMR Spectra

The parent compound $RuCl_2(PPh_3)_3$ is an unusual example of 5-coordinate Ru(II). The X-ray crystal structure analysis of this complex[8] shows that it is pentacoordinated having distorted square based pyramidal geometry. The two chlorine atoms and the two molecules of triphenylphosphine in the basal plane are trans to each other whereas the third triphenylphosphine is the apical one. The next closest approach to the ruthenium, in the position trans to the apical phosphorus atom, is made by hydrogen atom on a β-carbon of a phenyl ring; the metal hydrogen distance is approximately 2.59 Å, but there is no evidence for a metal-hydrogen interaction. Thus, the compound is a true pentacoordinated species, and that its stability arises from intramolecular

blocking of the unused octahedral site by the phenyl ring.

With title ligands, it gives compounds of the general formula $[RuCl_2(ligand)_2(PPh_3)].xCH_2Cl_2$ (x = 0, 1/2 or 1). These Ru(II) complexes seem to retain the structural characteristics of the parent compound, i.e., $RuCl_2(PPh_3)_3$. The ligands behave as monodentate through carbonyl oxygen. The β-hydrogen of third triphenylphosphine trans to carbonyl oxygen of the ligand is responsible for stability of the complexes due to blocking of the sixth position resulting in a quasi-octahedral structure. The monodentate nature of the ligands through oxygen is established by the following i.r. spectral shifts:

i) The $\nu_{C=O}$ of the ligands shift to lower wave number by 10-50 cm^{-1}. This band in the complexes either becomes broad or splits into two bands. This observation indicates that both ligand molecules are in cis-position in the complexes.

ii) The thioamide band IV and $\nu_{C=S}$ band shift to higher wave number (10-25 cm^{-1}) ruling out the possibility of coordination through S.

iii) The thioamide band I goes higher by (15-30 cm^{-1}) hence coordination through N is unlikely. There are unsystematic shifts in the position of thioamide bands II and III for drawing any significant inferences.

iv) All the characteristic peaks of triphenylphosphine[9] were present in the spectra of all the complxes.

The n.m.r. spectra of the complexes showed the proton resonance of dichloromethane at δ5.3-5.4 and all the characteristic signals of concerned ligands (Table V.3).

V.2.3 $[(\eta^5\text{-}C_5H_5)RuCl(ligand)(AsPh_3)].xCH_2Cl_2$ (x = 0, 1/2; ligands = Hctt, Hcept, Hcapt, Hcppt, Htp)

V.2.3.1 IR Spectra

In all these compounds $\nu_{C=O}$ goes down [$\Delta\nu_{C=O}$ = 15 (Hctt); 25 (Hcept), 65 and 30 (Hcapt); 60 and 20 (Hcppt) and 10 cm^{-1} (Htp)]. ν_{NH} disappears and a new strong band at 2360 cm^{-1} (2340 cm^{-1} in case of $[(\eta^5\text{-}C_5H_5)RuCl(Hcppt)(AsPh_3)]$ and $[(\eta^5\text{-}C_5H_5)\text{-}RuCl(Hcapt)(AsPh_3)].1/2\ CH_2Cl_2$, 2350 cm^{-1} in case of $[(\eta^5\text{-}C_5H_5)\text{-}RuCl(Htp)(AsPh_3)].1/2\ CH_2Cl_2$ appears indicating the presence of ligand in thiol form in the final product. The value for ν_{SH} is relatively smaller, it could be possibly because of stronger intermolecular hydrogen bonding. Four thioamide bands and $\nu_{C=S}$ of ligands are not descernible, one could conclude from the above shifts that there is a coordination through carbonyl oxygen in all the cases. Band at 1585 cm^{-1} ($\nu_{C=N}$) in case of $[(\eta^5\text{-}C_5H_5)\text{-}RuCl(Hctt)(AsPh_3)].1/2\ CH_2Cl_2$ shifts to higher value 1600 cm^{-1}. In case of $[(\eta^5\text{-}C_6H_5)RuCl(Hcapt)(AsPh_3)]$ band at 1730 cm^{-1} ($\nu_{C=O}$) goes to 1665 cm^{-1} indicating the ligand as monodentate one through carbonyl oxygen but surprisingly only in this case ligand seems to be present in the thione form rather than in thiol form after complexation.

V.2.4 [(η^5-C_5H_5)RuCl(ligand)($AsPh_3$)].1/2 CH_2Cl_2 (ligands = Hcpt, Hcett or Htpq)

V.2.4.1 IR Spectra

In all these complexes ν_{NH} and $\nu_{C=S}$ disappear $\nu_{C=O}$ remains almost invarient or goes up by +5 cm^{-1} which indicates exclusion of carbonyl oxygen as one of the donor sites. A new band at 2360 cm^{-1} appears which is tentatively assigned to ν_{SH} indicating presence of ligands in the thiol form after complexation. Low value of ν_{SH} may be attributed to intermolecular and/or intramolecular hydrogen bonding. SH group generally coordinates to metal ions after deprotonation, hence under the situations nitrogen appears to be the most potential donor site.

All the characteristic bands of PPh_3 and η^5-C_5H_5 (820-850 cm^{-1})[10] were present in the i.r. spectra of the complexes. The new bands of medium intensity in region of 350-480 cm^{-1} may be attributed to coupled vibration of ν(Ru-Cl), ν(Ru-O) or ν(Ru-N).

The proton n.m.r. spectra (Table V.3) of the complexes display a sharp singlet 4.1-4.3 (for η^5-C_5H_5) apart from all characteristic signals of concerned ligands and PPh_3. However, the NH proton resonance could not be detected in the n.m.r. spectra of the complexes.

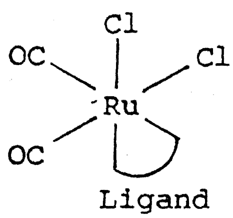
V.2.5 Electronic Spectra

The electronic spectra of ligands and complexes were taken in CH_2Cl_2, the band positions and their assignments are given in Table V.3.

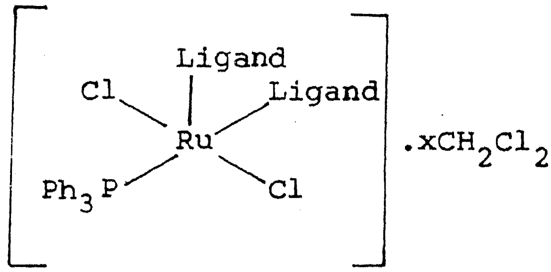
The ground state of ruthenium(II) in octahedral complexes is $^1A_{1g}$ and the excited states are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Therefore one would expect four transition bands due to transition from $^1A_{1g}$ to $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ but as transitions $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^3T_{2g}$ are spin forbidden (singlet $\rightarrow$ triplet), they are too weak to be observed and only two spin allowed transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ or $^1T_{2g}$ are expected. In our case the electronic spectra of the complexes showed continuous absorption in the visible region, therefore, some of d-d transitions were probably masked by this continuous absorption or by charge transfer (CT) or intraligand (IL) bands. The band in the region 465-485 nm may be assigned to $^1A_{1g} \rightarrow {}^1T_{2g}$ and in the region 500-600 nm may be due to $^1A_{1g} \rightarrow {}^1T_{1g}$. Some of the intraligand (IL) bands were present in electronic spectra of respective complexes with small shifts. The intense bands at 240-245 nm and 270-280 nm are assigned to charge transfer transition.

The diamagnetism of Ru(II), d^6 systems indicate the spin pairing, hence distorted octahedral structure,[11] assuming that η^5-C_5H_5 group occupies three coordination sites, is preferred over tetrahedral or distorted tetrahedral as spin pairing is not possible in later cases. Thus, on the basis of analytical,

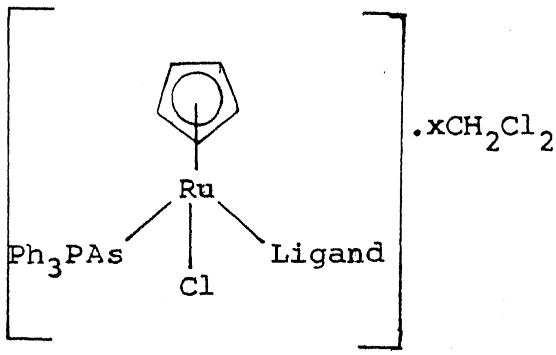
spectral (i.r., u.v., visible and ^{1}H n.m.r.) and magnetic moments data, the following structures are proposed for the complexes:



Distorted octahedral



Sqare-pyramidal
(quasi-octahedral)



Distorted octahedron

(ligand = Hctt, Hcept, Hcpt, Hcett, Hcapt, Hcppt, Htp or Htpq);
(X = 0, 1/2 or 1)

Table V.1. Analytical data of the complexes

Compound	Colour	M.P. (^{o}C)	Yield (%)	% Found (Calcd)						Possibl coordi- nation
				C	H	N	Cl	S	P	
1	2	3	4	5	6	7	8	9	10	11
[$RuCl_2(CO)_2(Hctt)$]	Yellowish brown	200	31	34.4 (34.6)	2.6 (2.9)	3.3 (3.1)	15.9 (15.7)	7.3 (7.1)	-	N and S
[$RuCl_2(CO)_2(Hcept)$]	Brown	170	66	28.4 (28.2)	2.5 (2.3)	6.8 (6.6)	16.9 (16.7)	7.7 (7.5)	-	S and O
[$RuCl_2(CO)_2(Hcpt)$]	Brown	$>$200d	42	28.5 (28.2)	2.4 (2.3)	6.8 (6.6)	16.8 (16.7)	7.8 (7.5)	-	N and S
[$RuCl_2(CO)_2(Hcett)$]	Reddish brown	$>$200d	36	27.3 (27.1)	2.3 (2.1)	3.5 (3.2)	16.2 (16.0)	14.6 (14.4)	-	N and S
[$RuCl_2(CO)_2(Hcapt)$]	Brown	$>$200d	25	24.5 (24.2)	2.1 (1.8)	10.8 (10.6)	18.2 (17.9)	8.4 (8.1)	-	N and O
[$RuCl_2(CO)_2(Hcppt)$]	Yellowish brown	185-190	43	35.7 (35.5)	2.6 (2.3)	9.0 (8.9)	15.3 (15.0)	6.9 (6.8)	-	N and O
[$RuCl_2(CO)_2(Htp)$]	Reddish brown	100	20	25.5 (25.3)	1.5 (1.0)	7.6 (7.4)	18.9 (18.7)	8.6 (8.4)	-	N and S
[$RuCl_2(CO)_2(Htpq)$]	Light yellow	200	58	39.6 (39.8)	1.9 (2.1)	5.5 (5.8)	14.9 (14.7)	6.8 (6.6)	-	N and S
[$RuCl_2(Hctt)_2(PPh_3)$]-1/2 CH_2Cl_2	Maroon	130-135	77	52.9 (52.7)	4.8 (4.6)	3.2 (3.0)	11.7 (11.5)	7.1 (6.9)	3.5 (3.4)	O

Table V.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11
$[RuCl_2(Hcept)_2(PPh_3)]$	Maroon	135-140	93	49.3 (49.2)	4.3 (4.2)	6.9 (6.7)	8.8 (8.6)	7.9 (7.7)	3.5 (3.7)	O
$[RuCl_2(Hcpt)_2(PPh_3)]$	Dirty yellow	120	68	49.4 (49.2)	4.3 (4.2)	6.9 (6.7)	8.8 (8.6)	7.8 (7.7)	3.8 (3.7)	O
$[RuCl_2(Hcett)_2(PPh_3)]$	Violet	135	78	47.4 (47.2)	3.9 (3.8)	3.3 (3.2)	8.4 (8.2)	14.9 (14.8)	3.8 (3.6)	O
$[RuCl_2(Hcapt)_2(PPh_3)]$	Brick red	170-172	62	46.8 (46.6)	3.9 (3.8)	11.1 (10.9)	9.4 (9.2)	8.4 (8.3)	4.2 (4.0)	O
$[RuCl_2(Hcppt)_2(PPh_3)]$-1/2 CH_2Cl_2	Maroon	145-150	45	52.9 (52.8)	4.1 (3.9)	8.9 (8.7)	11.2 (11.0)	6.7 (6.6)	3.4 (3.2)	O
$[RuCl_2(Htp)(PPh_3)]$-CH_2Cl_2	Bluish violet	170	46	45.4 (45.2)	3.2 (3.0)	6.9 (6.8)	17.3 (17.2)	7.9 (7.8)	3.9 (3.8)	O
$[RuCl_2(Htpq)_2(PPh_3)]$	Yellow	180	50	58.8 (58.6)	3.9 (3.7)	6.1 (5.9)	7.7 (7.5)	6.9 (6.8)	3.4 (3.3)	O
$[(\eta^5-C_5H_5)RuCl(Hctt)$-$(AsPh_3)\cdot 1/2\ CH_2Cl_2$	Yellow brown	105-110	25	53.8 (53.6)	4.6 (4.4)	1.6 (1.8)	9.2 (9.5)	4.4 (4.1)	-	O
$[(\eta^5-C_5H_5)RuCl(Hcept)$-$(AsPh_3)\cdot 1/2\ CH_2Cl_2$	Maroon	85	34	50.6 (50.5)	4.3 (4.1)	3.7 (3.7)	9.7 (9.5)	4.4 (4.3)	-	O
$[(\eta^5-C_5H_5)RuCl(Hcpt)$-$(AsPh_3)\cdot 1/2\ CH_2Cl_2$	Grey	155	67	50.7 (50.5)	4.2 (4.1)	3.6 (3.7)	9.6 (9.5)	4.5 (4.3)	-	N

...contd.

Table V.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11
$[(\eta^5-C_5H_5)RuCl(Hcett)-(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	Violet	92-95	60	49.5 (49.4)	3.8 (3.9)	1.9 (1.8)	9.5 (9.3)	8.6 (8.4)	-	N
$[(\eta^5-C_5H_5)RuCl(Hcapt)-(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	Reddish violet	170	20	49.4 (49.2)	4.0 (3.9)	5.9 (5.8)	10.1 (9.9)	4.6 (4.4)	-	O
$[(\eta^5-C_5H_5)RuCl(Hcapt)-(AsPh_3)]$	Orange	180	67	51.6 (51.4)	4.2 (4.0)	6.5 (6.2)	5.4 (5.2)	4.9 (4.7)	-	O
$[(\eta^5-C_5H_5)RuCl(Hcppt)-(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	Dark violet	115-120	47	53.7 (53.6)	4.1 (4.0)	5.5 (5.3)	8.8 (8.9)	4.2 (4.0)	-	O
$[(\eta^5-C_5H_5)RuCl(Hcppt)-(AsPh_3)]$	Orange	172-175	26	56.1 (55.9)	4.3 (4.1)	5.8 (5.6)	4.8 (4.7)	4.3 (4.2)	-	O
$[(\eta^5-C_5H_5)RuCl(Htp)-(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	Violet	82-85	45	50.6 (50.4)	3.8 (3.6)	4.2 (4.0)	10.3 (10.1)	4.8 (4.6)	-	O
$[(\eta^5-C_5H_5)RuCl(Htpq)-(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	Yellow	125-130	43	56.2 (56.0)	4.1 (3.9)	3.7 (3.5)	8.9 (8.8)	4.2 (4.0)	-	N

Table V.2. Major i.r. bands of interest. Comparison of i.r. spectra of the complexes with ligand (cm^{-1})

Compounds	ν(NH)	ν(C≡O)	ν(C=O)	ν(C=S)	Thioamide bands			
					I	II	III	IV
1	2	3	4	5	6	7	8	9
[Hctt]	3220	-	1765s	1130s	1540s	1360s	1075s	850m
[$RuCl_2(CO)_2$(Hctt)]	-	2100s 2040s	1770s	1115m	1500s	1320m	1060s	840m
[Hcept]	3350m 3325m	-	1765s	1120s	1540s	1340s	1070s	870m
[$RuCl_2(CO)_2$(Hcept)]	-	2140m 2080s	1745s	1100m	1555s	1385s	1070s	865m
[Hcpt]	3210m	-	1730s	1125s	1500s	1320s	1015s	880s
[$RuCl_2(Co)_2$(Hcpt)]	-	2100 2020	1790s	1115s	1480s	1310s	1010m	860s
[Hcett]	3240s,br	-	1730s	1180s,br	1510s	1360s	1020s	770s
[$RuCl_2(CO)_2$(Hcett)]	3500- 3100br	2060s 1990s	1750m	1150m	1500s	1345s	1000m	720s
[Hcapt]	3400 3370 3250	-	1730s	1120s	1580s	1330s	1060s	845s
[$RuCl_2(CO)_2$(Hcapt)]	-	2080s 2020s	1690s	1130m	1550s	1310s	1070s	860s

...contd.

Table V.2 (contd.)

1	2	3	4	5	6	7	8	9
[Hcppt]	3410m 3260m 3160m	-	1720s	1125s	1520s	1350s	1000m	860m
[$RuCl_2(CO)_2$(Hcppt)]	-	2100s 2020s	1680s	1140m	1510s	1320s	1010m	870m
[Htp]	3200m	-	1765s	1145s	1555s	1305s	1000m	850m
[$RuCl_2(Co)_2$(Htp)]	3100m	2040s 1980s	1770s	1135s	1540m	-	990m	810s
[Htpq]	3250m	-	1660s	-	1540s	1345s	1000m	770s
[$RuCl_2(CO)_2$(Htpq)]	3400br	2100s 2020s	1680s	-	1530s	1330s	980m	750s

Table V.3. Electronic spectra of the ligands and the complexes in CH_2Cl_2 and ^1H NMR spectra of the complexes in $CDCl_3$

Compound	Band position λ_{max} (nm)	Assignment	NMR signals with assignments (δ)
1	2	3	4
[Hctt]	450	$n \rightarrow \pi^*$	
	310	$\pi \rightarrow \pi^*$	
	270	IL CT	
[Hcept]	440	$n \rightarrow \pi^*$	
	365	$\pi \rightarrow \pi^*$	
[Hcpt]	300	$n \rightarrow \pi^*$	
	262	$\pi \rightarrow \pi^*$	
[Hcett]	350	$n \rightarrow \pi^*$	
	292	$\pi \rightarrow \pi^*$	
[Hcapt][a]	350	$\pi \rightarrow \pi^*$	
	290	CT	
[Hcppt][a]	415	$n \rightarrow \pi^*$	
	390	$\pi \rightarrow \pi^*$	
	360	CT	
[Htp][a]	370	$n \rightarrow \pi^*$	
	330	$\pi \rightarrow \pi^*$	
	285	CT	

Table V.3. Electronic spectra of the ligands and the complexes in CH_2Cl_2 and ^1H NMR spectra of the complexes in $CDCl_3$

Compound	Band position λ_{max} (nm)	Assignment	NMR signals with assignments (δ)
1	2	3	4
[Hctt]	450	$n \rightarrow \pi^*$	
	310	$\pi \rightarrow \pi^*$	
	270	IL CT	
[Hcept]	440	$n \rightarrow \pi^*$	
	365	$\pi \rightarrow \pi^*$	
[Hcpt]	300	$n \rightarrow \pi^*$	
	262	$\pi \rightarrow \pi^*$	
[Hcett]	350	$n \rightarrow \pi^*$	
	292	$\pi \rightarrow \pi^*$	
[Hcapt][a]	350	$\pi \rightarrow \pi^*$	
	290	CT	
[Hcppt][a]	415	$n \rightarrow \pi^*$	
	390	$\pi \rightarrow \pi^*$	
	360	CT	
[Htp][a]	370	$n \rightarrow \pi^*$	
	330	$\pi \rightarrow \pi^*$	
	285	CT	

..contd.

Table V.3 (contd.)

1	2	3	4
[Htpq][b]	295	$\pi \rightarrow \pi^*$	
	262	$\pi \rightarrow \pi^*$	
$[RuCl_2(CO)_2(Hctt)]$	350	IL	1.3 (t, 3 H, $-CH_3$), 2.0 (s, 3 H, $-CH_3$ ring), 4.2 (s, 2 H, $-CH_2$), 7.3 (s, 4 H, aromatic)
	245	CT	
$[RuCl_2(CO)_2(Hcept)]$	335br	IL	1.4 (t, 3 H, $-CH_3$), 4.3 (s, 2 H, $-CH_2$), 6.7-7.2 (m, 3 H, pyrrolyl CH), 8.3 (s, 1 H, imide NH)
	245	CT	
$[RuCl_2(CO)_2(Hcpt)]$	340	IL	
	240	CT	
$[RuCl_2(CO)_2(Hcett)]$	430br	$^1A_{1g} \rightarrow {}^1T_{2g}$	
	350sh	IL	
	245	CT	
$[RuCl_2(CO)_2(Hcapt)]$	355	IL	
	235	CT	
$[RuCl_2(CO)_2(Hcppt)]$	330br	IL	6.7-7.8 (m, aromatic)
	245	CT	
$[RuCl_2(CO)_2(Htp)]$	440Br	$^1A_{1g} \rightarrow {}^1T_{2g}$	
	315	IL	
	255	IL	

Table V.3 (contd.)

1	2	3	4
[$RuCl_2(CO)_2$(Htpq)]	305br	IL	
	240	CT	
[$RuCl_2$(Hctt)$_2$(PPh_3)]-1/2 CH_2Cl_2	500 ($6.17x10^5$)	$^1A_{1g} \rightarrow {}^1T_{1g}$	1.3 (t, 6 H, $-CH_3$), 2.3 (s, 6 H, $-CH_3$ ring), 4.1 (q, 4 H, $-OCH_2$), 5.3 (s, 1 H, $-CH_2Cl_2$), 7.2-7.4 (m, 26 H, aromatic)
	268sh	IL	
	236 ($3.32x10^4$)	CT	
[$RuCl_2$(Hcept)$_2$(PPh_3)]	448 ($4.48x10^5$)	$^1A_{1g} \rightarrow {}^1T_{2g}$	1.3 (t, 6 H, $-CH_3$), 4.2 (q, 4H, $-OCH_2$), 6.7-7.0 (m, 24 H, aromatic)
	356 ($9.72x10^5$)	IL	
	264sh	IL	
	234 ($2.45x10^4$)	CT	
[$RuCl_2$(Hcpt)$_2$(PPh_3)]	580	$^1A_{1g} \rightarrow {}^1T_{1g}$	
	372sh	IL	
	280	IL	
	236	CT	
[$RuCl_2$(Hcett)$_2$(PPh_3)]	560br	$^1A_{1g} \rightarrow {}^1T_{1g}$	
	332sh	IL	
	272sh	CT	
	238 ($2.69x10^4$)	CT	
[$RuCl_2$(Hcapt)$_2$(PPh_3)]	460br ($5.42x10^5$)	$^1A_{1g} \rightarrow {}^1T_{1g}$	
	348 ($1.12x10^4$)	IL	
	280sh	IL	

Table V.3 (contd.)

1	2	3	4
[$RuCl_2(Hcppt)_2(PPh_3)$]-1/2 CH_2Cl_2	456	$^1A_{1g} \rightarrow {}^1T_{2g}$	5.3 (s, 1 H, $-CH_2Cl_2$), 7.4 (br, 34 H, aromatic)
	356	IL	
	238	CT	
[$RuCl_2(Htp)_2(PPh_3)$]-CH_2Cl_2	532	$^1A_{1g} \rightarrow {}^1T_{1g}$	5.3 (s, 2 H, $-CH_2Cl_2$), 7.4 (m, 21 H, aromatic)
	372	IL	
	234	CT	
[$RuCl_2(Htpq)_2(PPh_3)$]	460br	$^1A_{1g} \rightarrow {}^1T_{2g}$	
	340sh	IL	
	300	IL	
	234 (2.22×10^4)	CT	
[(η^5-C_5H_5)RuCl(Hctt)-($AsPh_3$)]·1/2 CH_2Cl_2	376br,sh	IL	1.3 (t, 3 H, $-CH_3$), 2.4 (s, 3 H, $-CH_3$ ring), 4.1 (s, 5 H, η^5-C_5H_5), 4.4 (q, 2 H, $-OCH_2$), 5.3 (s, 1 H, $-CH_2Cl_2$), 7.3 (m, 22 H, aromatic)
	238 (2.59×10^4)	CT	
[(η^5-C_5H_5)RuCl(Hcept)-($AsPh_3$)]·1/2 CH_2Cl_2	488sh	$^1A_{1g} \rightarrow {}^1T_{2g}$	1.3 (t, 3 H, $-CH_3$), 4.2 (m, 7 H, OCH_2, coupled with η^5-C_5H_5), 5.3 (s, 1 H, $-CH_2Cl_2$), 7.4 (m, 21 H, aromatic)
	360 (2.95×10^4)	IL	
	266sh	IL	
	240 (4.11×10^4)	CT	
[(η^5-C_5H_5)RuCl(Hcpt)-($AsPh_3$)]·1/2 CH_2Cl	364 (5.39×10^3)	IL	
	236 (6.58×10^3)	CT	

...contd.

Table V.3 (contd.)

1	2	3	4
[$(\eta^5$-$C_5H_5)RuCl(Hcett)$-$(AsPh_3)$]·1/2 CH_2Cl_2	460br,sh	$^1A_{1g} \rightarrow {}^1T_{2g}$	1.3 (t, 3 H, $-CH_3$), 4.2 (m, 7 H, OCH_2, Coupled with η^5-C_5H_5), 5.3 (s, 1 H, $-CH_2Cl_2$), 6.9-7.7 (m, 21H, aromatic)
	344sh	IL	
	236 (3.22×10^4)	CT	
[$(\eta^5$-$C_5H_5)RuCl(Hcapt)$-$(AsPh_3)$]·1/2 CH_2Cl_2	496 (3.14×10^3)	$^1A_{1g} \rightarrow {}^1T_{1g}$	4.2 (s, 5 H, η^5-C_5H_5), 5.3 (s, 1 H, $-CH_2Cl_2$), 7.3-7.7 (m, 21 H, aromatic).
	352 (9.83×10^3)	IL	
	272 (4.24×10^3)	IL	
	236 (1.42×10^4)	CT	
[$(\eta^5$-$C_5H_5)RuCl(Hcpt)$-$(AsPh_3)$]	472 (3.50×10^3)	$^1A_1 \rightarrow {}^1T_{2g}$	4.2 (s, 5 H, η^5-C_5H_5), 7.3-7.7 (m, 21 H, aromatic)
	358 (1.09×10^4)	IL	
	230 (1.98×10^4)	CT	
[$(\eta^5$-$C_5H_5)RuCl(Hcppt)$-$(AsPh_3)$]·1/2 CH_2Cl_2	460sh	$^1A_{1g} \rightarrow {}^1T_{2g}$	4.1 (s, 5 H, η^5-C_5H_5), 5.3 (s, 1 H, CH_2Cl_2), 7.4 (m, 26 H, aromatic)
	364 (1.07×10^4)	IL	
	240 (2.80×10^4)	CT	
[$(\eta^5$-$C_5H_5)RuCl(Hcppt)$-$(AsPh_3)$]	480br (4.54×10^3)	$^1A_{1g} \rightarrow {}^1T_{2g}$	4.1 (s, 5 H, η^5-C_5H_5), 7.3 (m, 26 H, aromatic)
	364 (1.81×10^4)	IL	
	234 (3.27×10^4)	CT	
[$(\eta^5$-$C_5H_5)RuCl(Htp)$-$(AsPh_3)$]·1/2 CH_2Cl_2	560br	$^1A_{1g} \rightarrow {}^1T_{1g}$	4.2 (s, 5 H, η^5-C_5H_5), 5.4 (s, 1 H, $-CH_2CH_2$), 7.3-7.9 (m, 21 H, aromatic)
	368sh	IL	
	256sh	CT	
	230 (1.89×10^4)	CT	

...contd.

Table V.3 (contd.)

1	2	3	4
$[(\eta^5-C_5H_5)RuCl(Htpq)-(AsPh_3)]\cdot 1/2\ CH_2Cl_2$	340sh	CT	
	296 (2.79×10^4)	IL	
	240 (4.11×10^4)	CT	

a) chloroform;

b) DMF

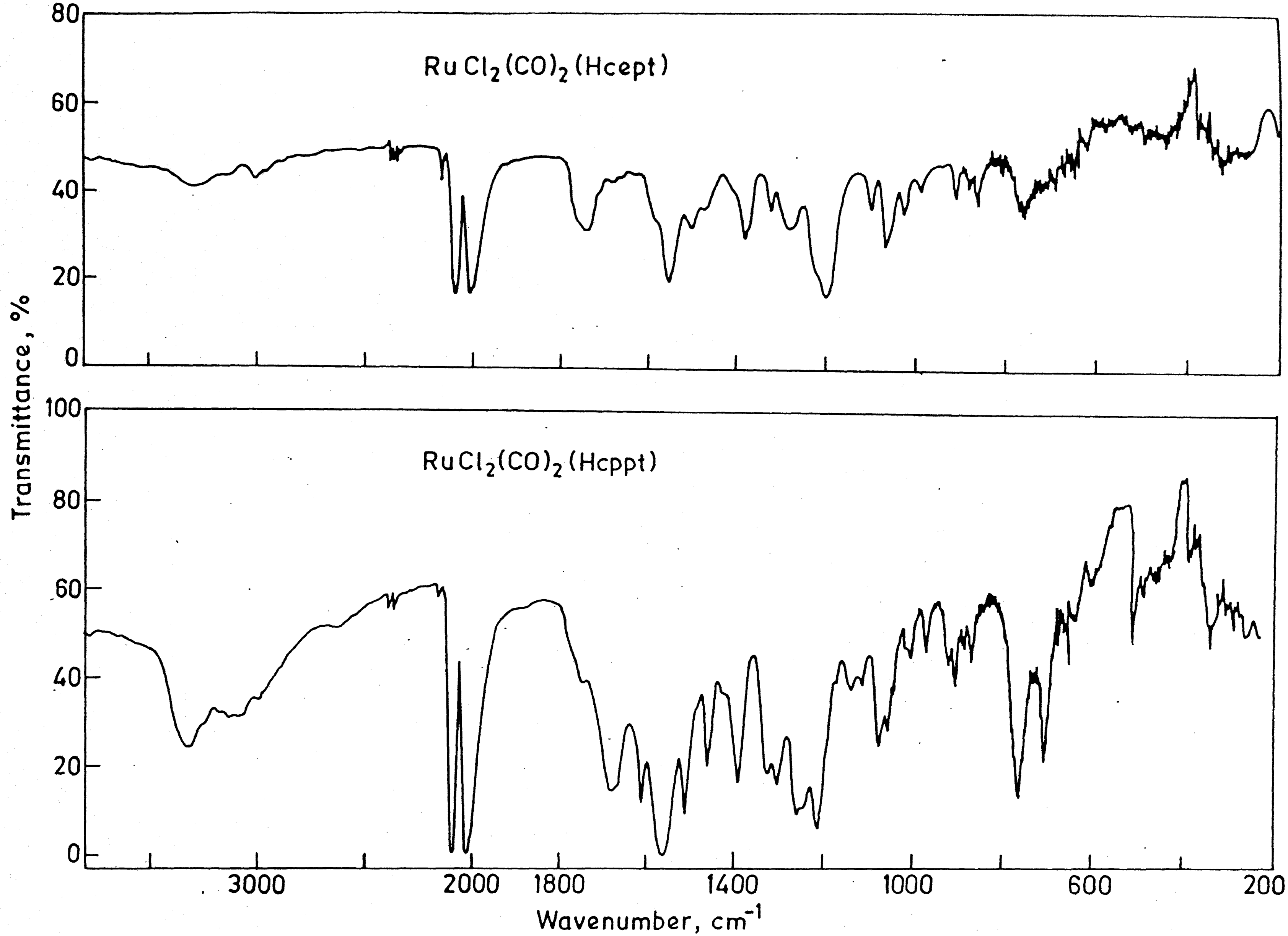
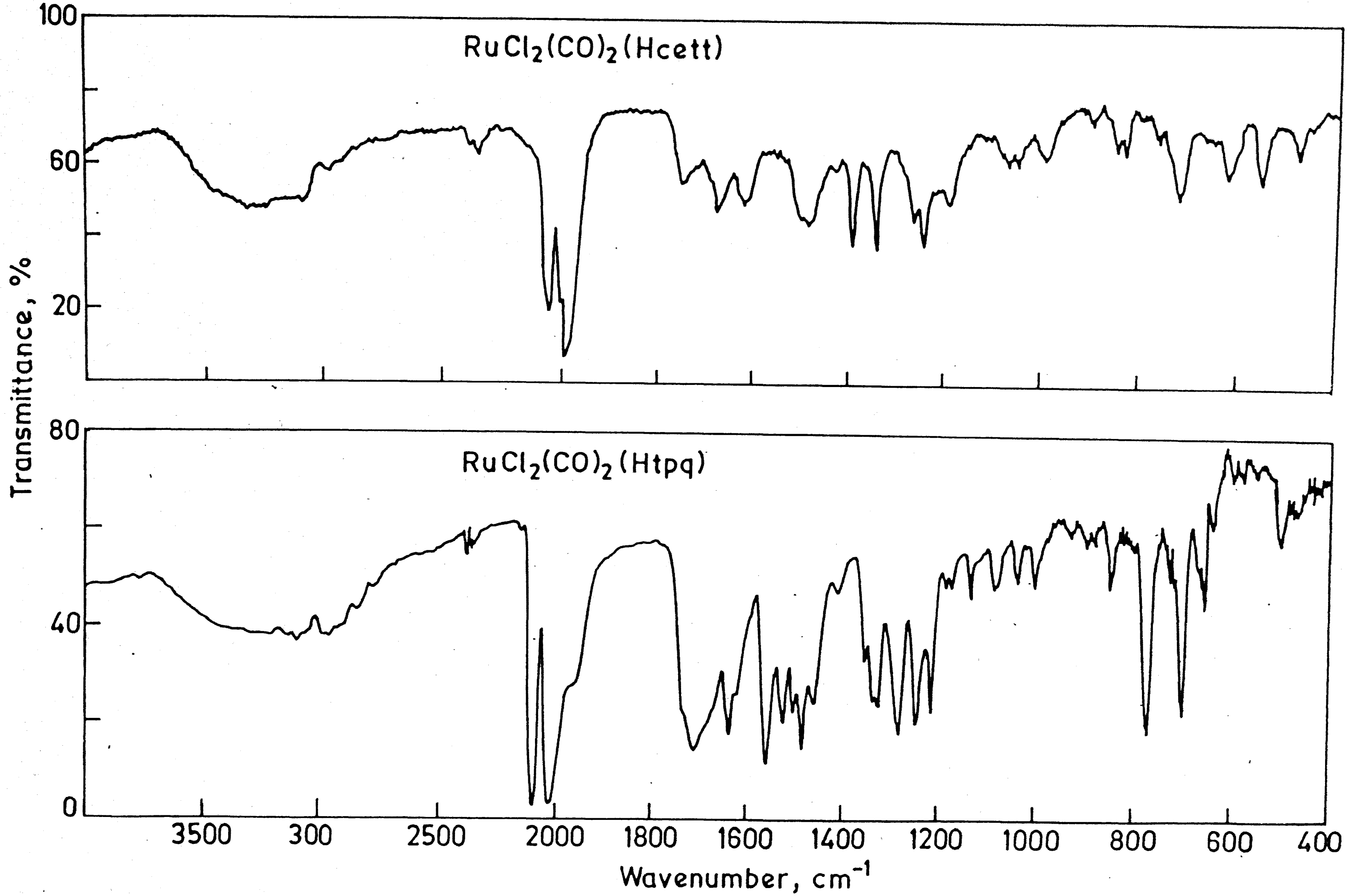
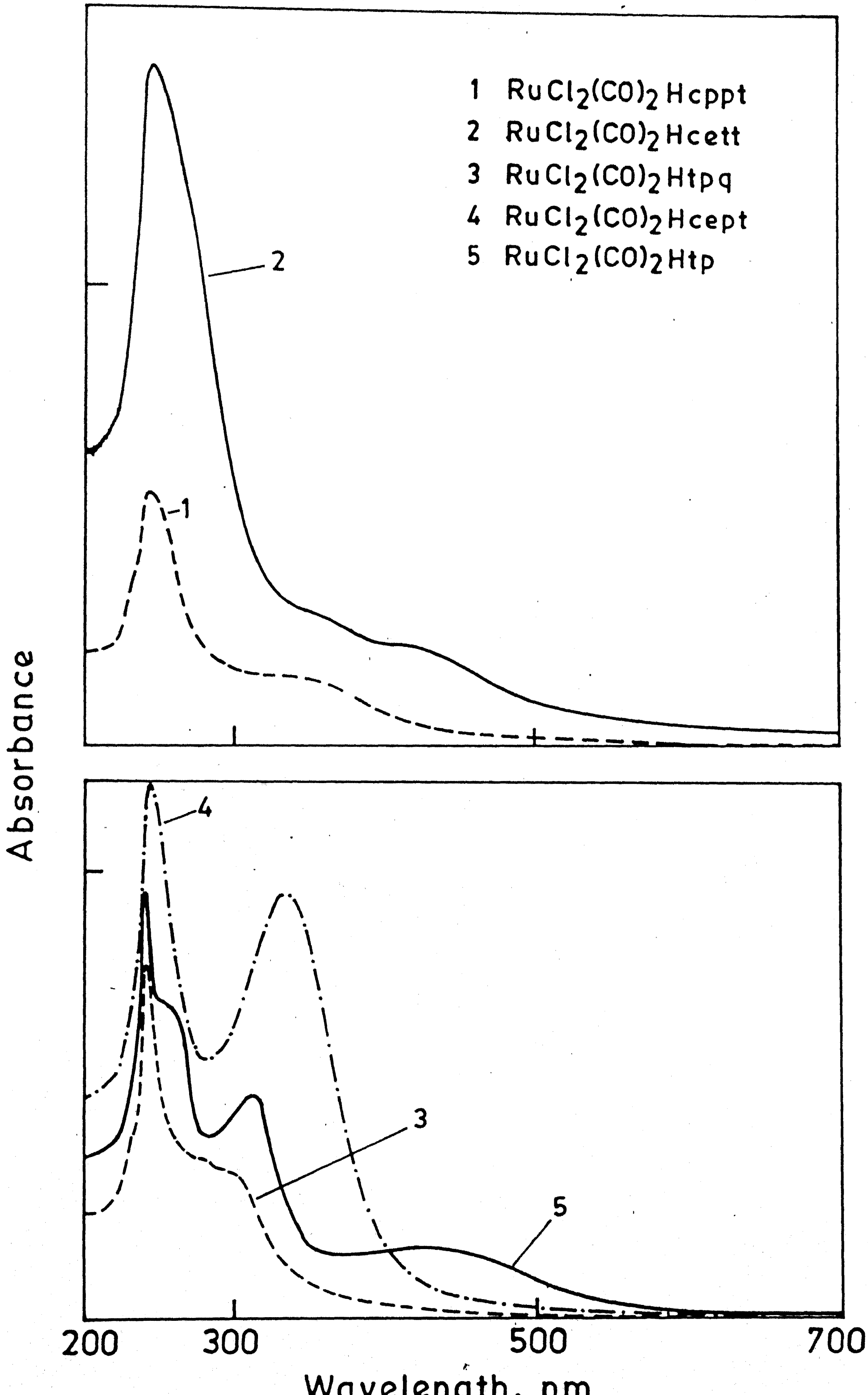

RuCl2(CO)2(Hcept)
RuCl2(CO)2(Hcppt)
Transmittance, %
80
60
40
20
0
100
80
60
40
20
0
3000
2000
1800
1400
1000
600
200
Wavenumber, cm-1

Fig. V. 1



RuCl2(CO)2(Hcett)
RuCl2(CO)2(Htpq)
Transmittance, %
100
60
20
80
40
0
3500
300
2500
2000
1800
1600
1400
1200
1000
800
600
400
Wavenumber, cm-1

Fig. V.2



1 $RuCl_2(CO)_2Hcppt$
2 $RuCl_2(CO)_2Hcett$
3 $RuCl_2(CO)_2Htpq$
4 $RuCl_2(CO)_2Hcept$
5 $RuCl_2(CO)_2Htp$
Absorbance
200
300
500
700
Wavelength, nm

Fig. V.3

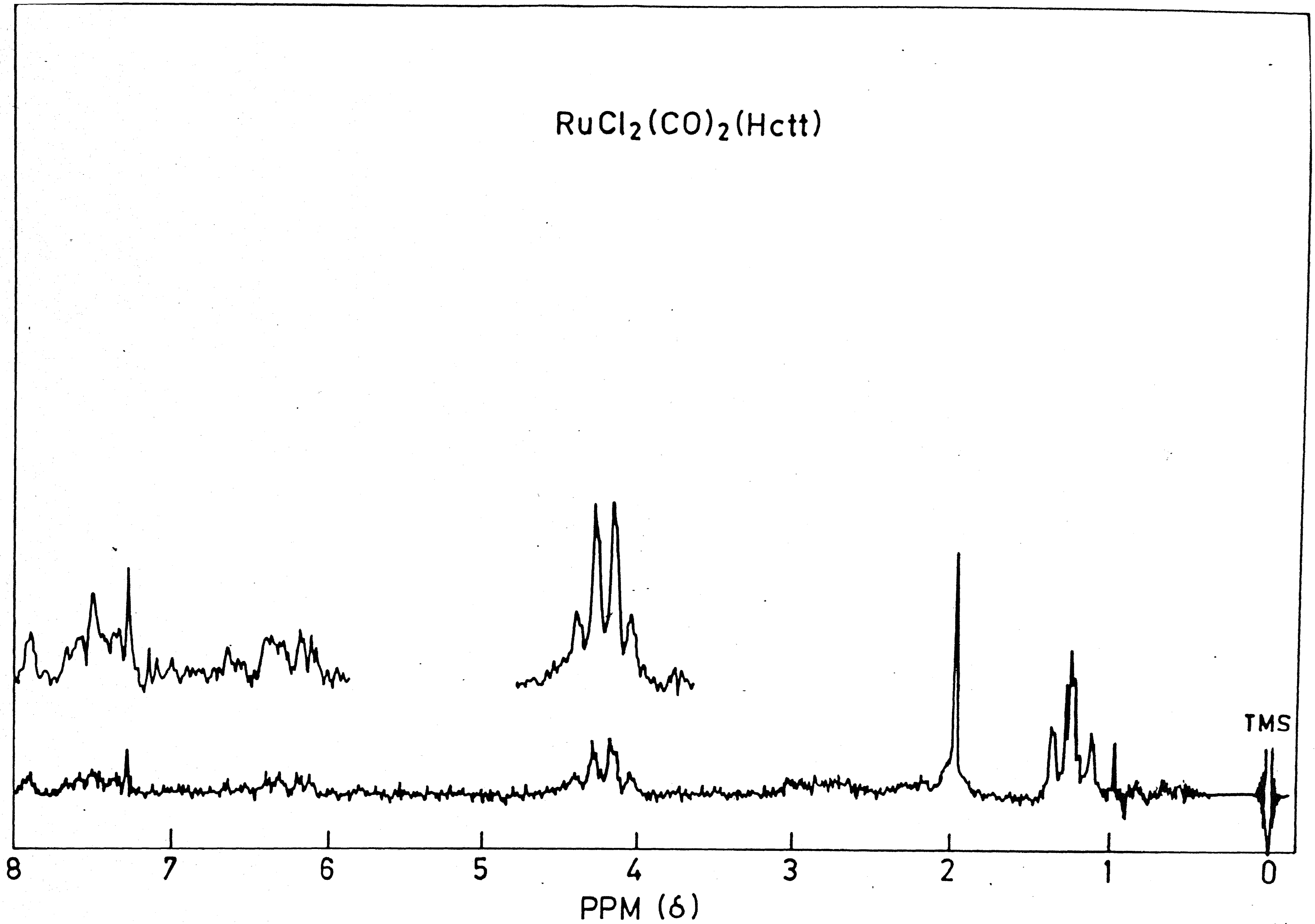


Fig. V

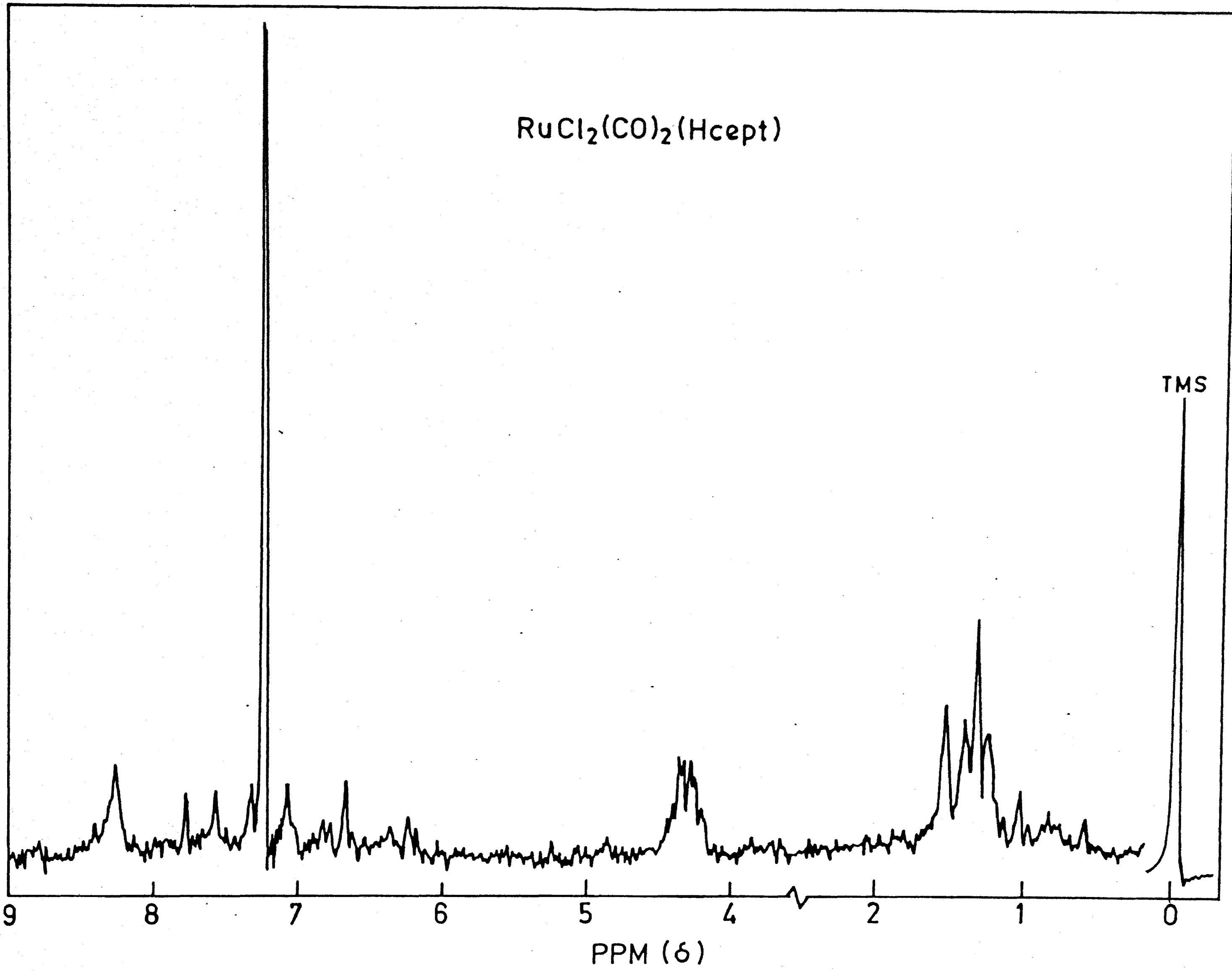
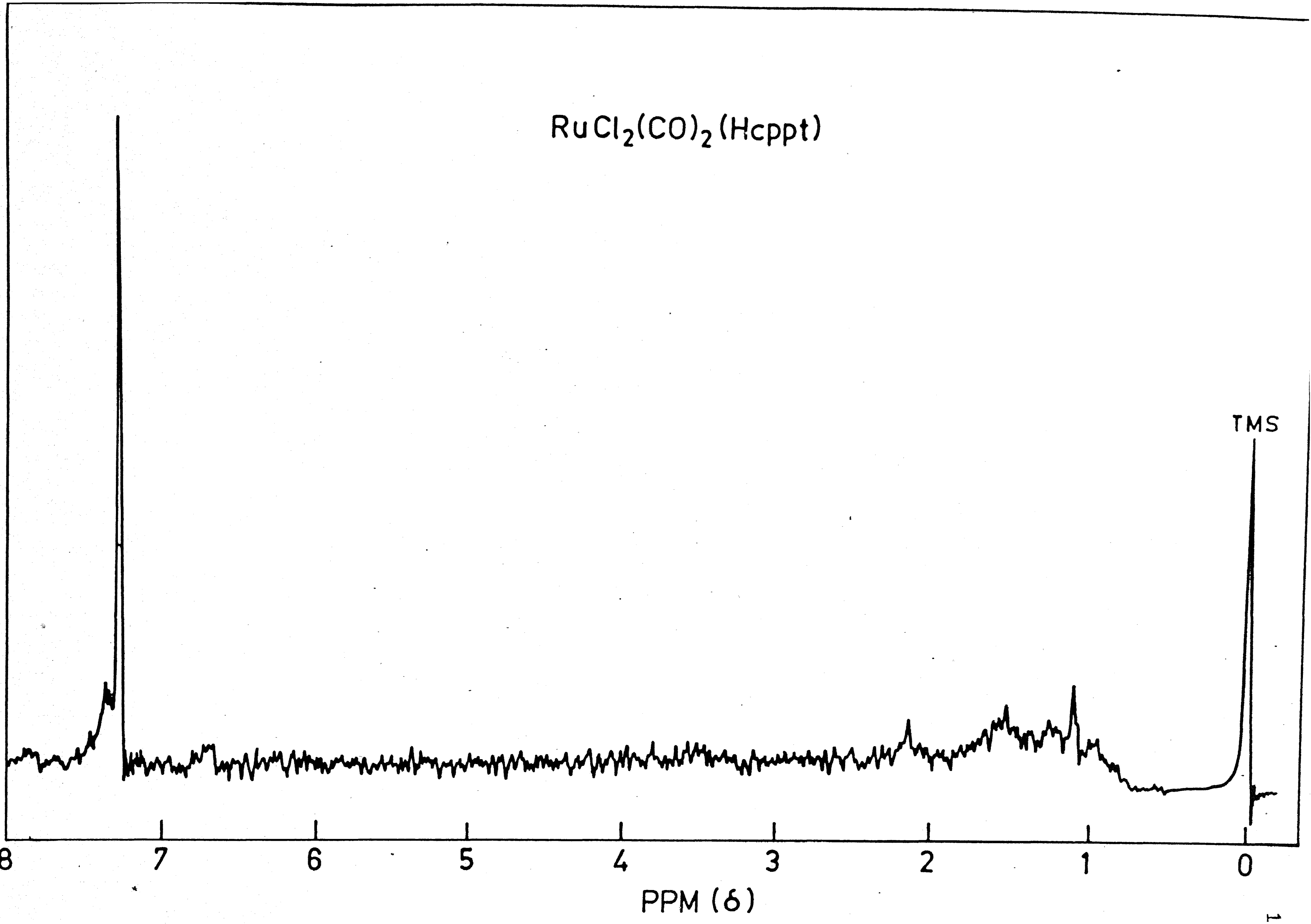
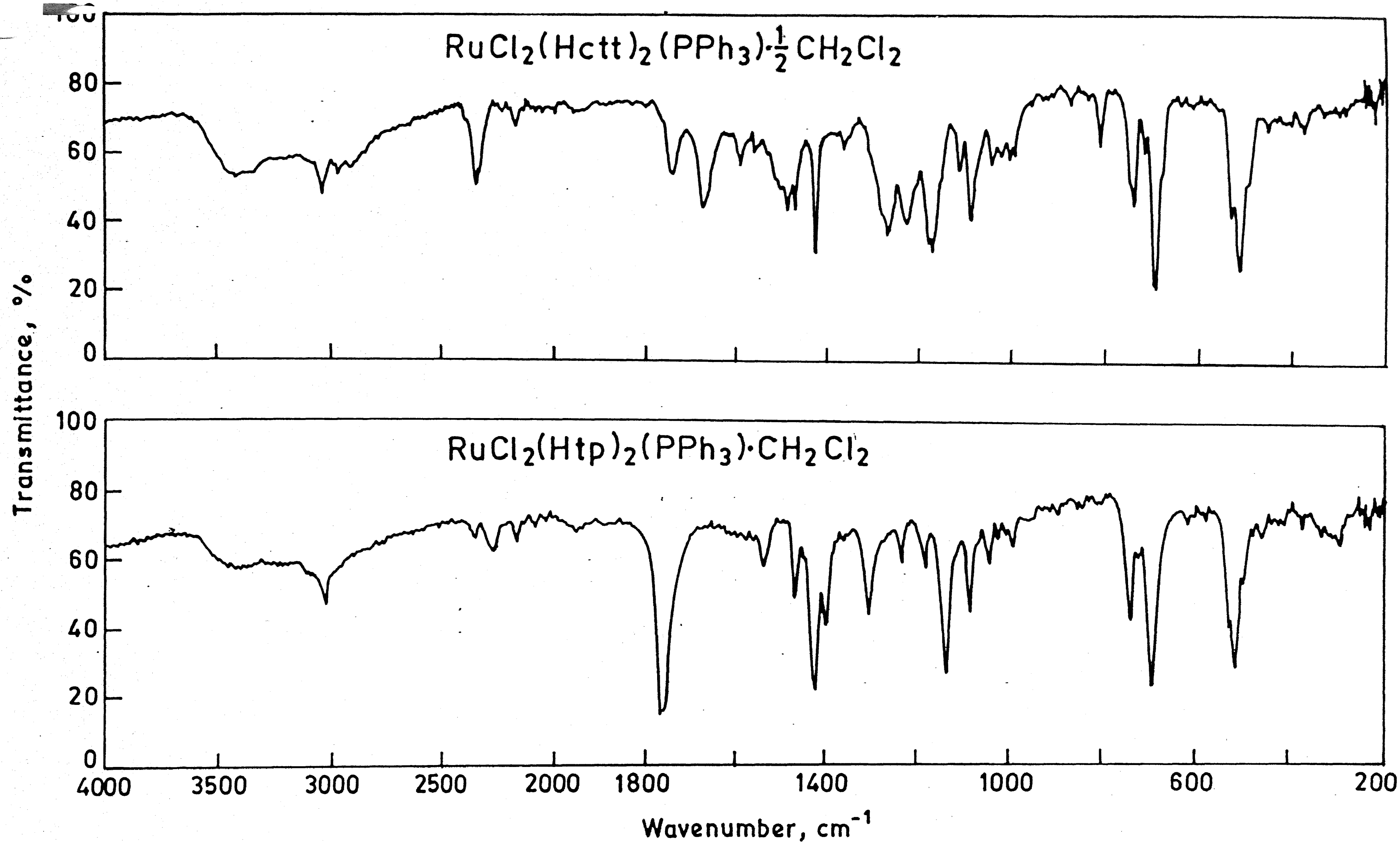


Fig. V.5



RuCl2(CO)2(Hcppt)
TMS
8
7
6
5
4
3
2
1
0
PPM (δ)



$RuCl_2(Hctt)_2(PPh_3)\cdot\frac{1}{2}CH_2Cl_2$
$RuCl_2(Htp)_2(PPh_3)\cdot CH_2Cl_2$
Transmittance, %
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1400
1000
600
200
Wavenumber, cm^{-1}

Fig. V.7

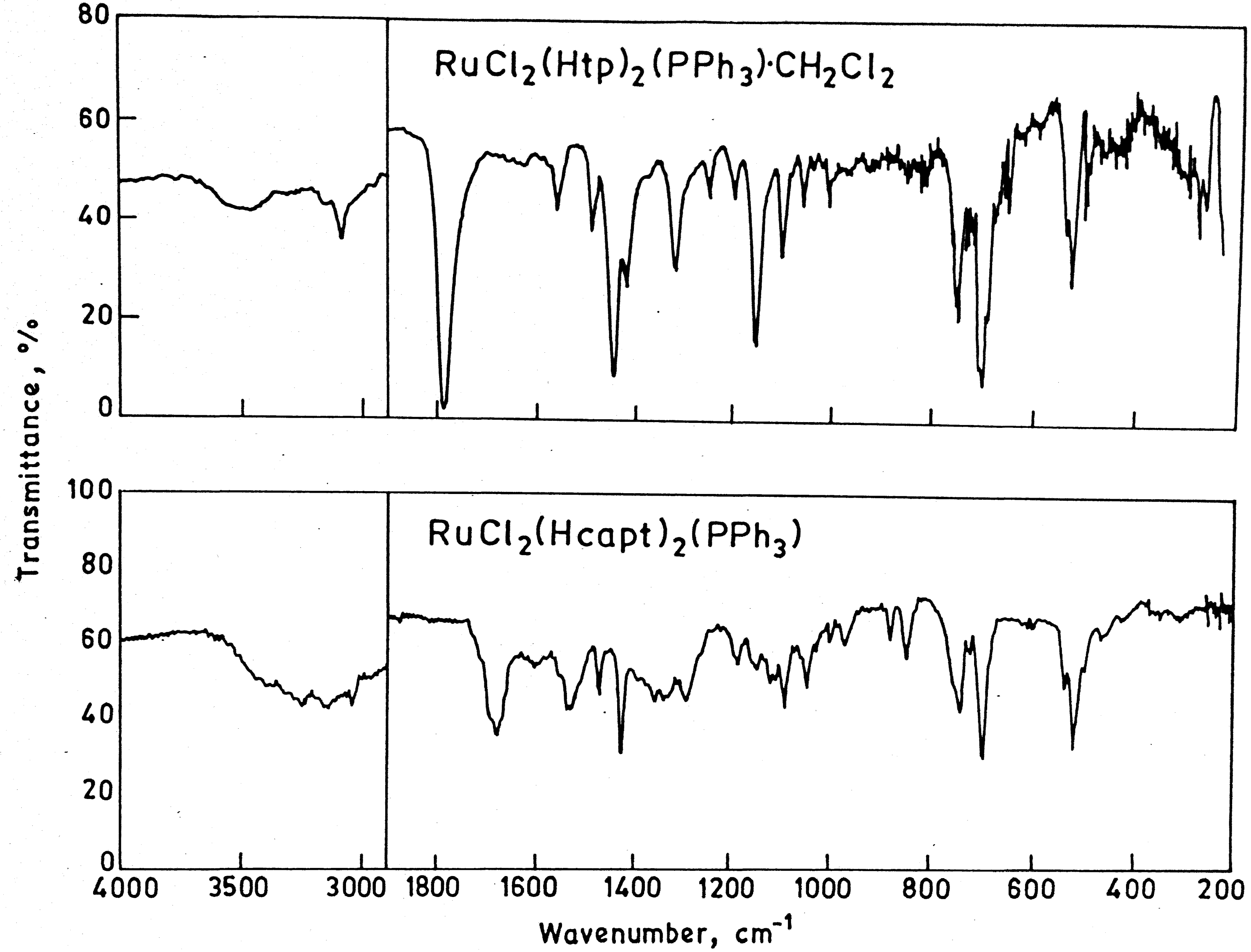
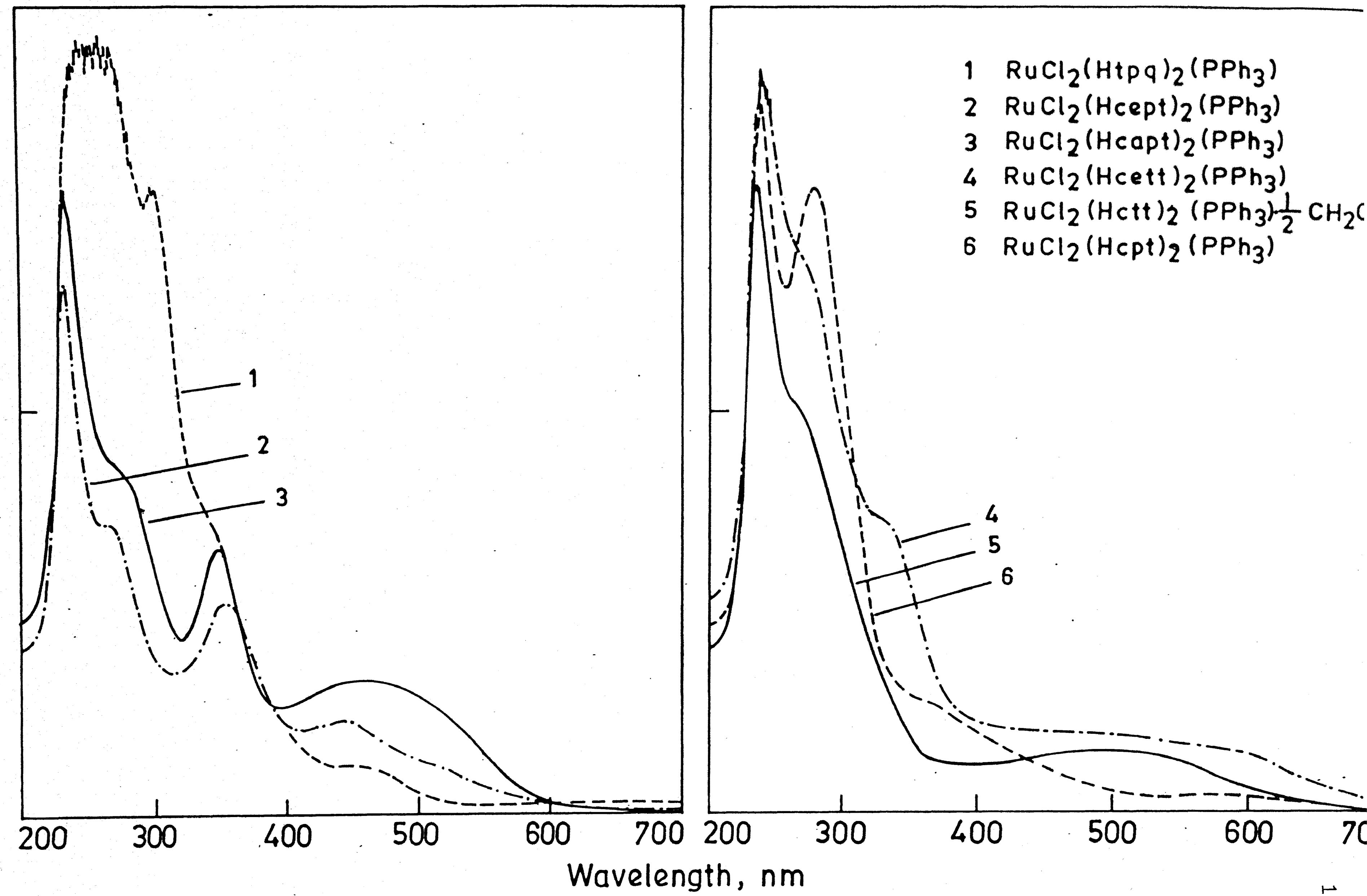

RuCl2(Htp)2(PPh3)·CH2Cl2
RuCl2(Hcapt)2(PPh3)
Transmittance, %
80
60
40
20
0
100
80
60
40
20
0
4000
3500
3000
1800
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm-1

Fig. V.8


1 RuCl2(Htpq)2(PPh3)
2 RuCl2(Hcept)2(PPh3)
3 RuCl2(Hcapt)2(PPh3)
4 RuCl2(Hcett)2(PPh3)
5 RuCl2(Hctt)2 (PPh3)·1/2 CH2C
6 RuCl2(Hcpt)2(PPh3)
1
2
3
4
5
6
200
300
400
500
600
700
200
300
400
500
600
70
Wavelength, nm

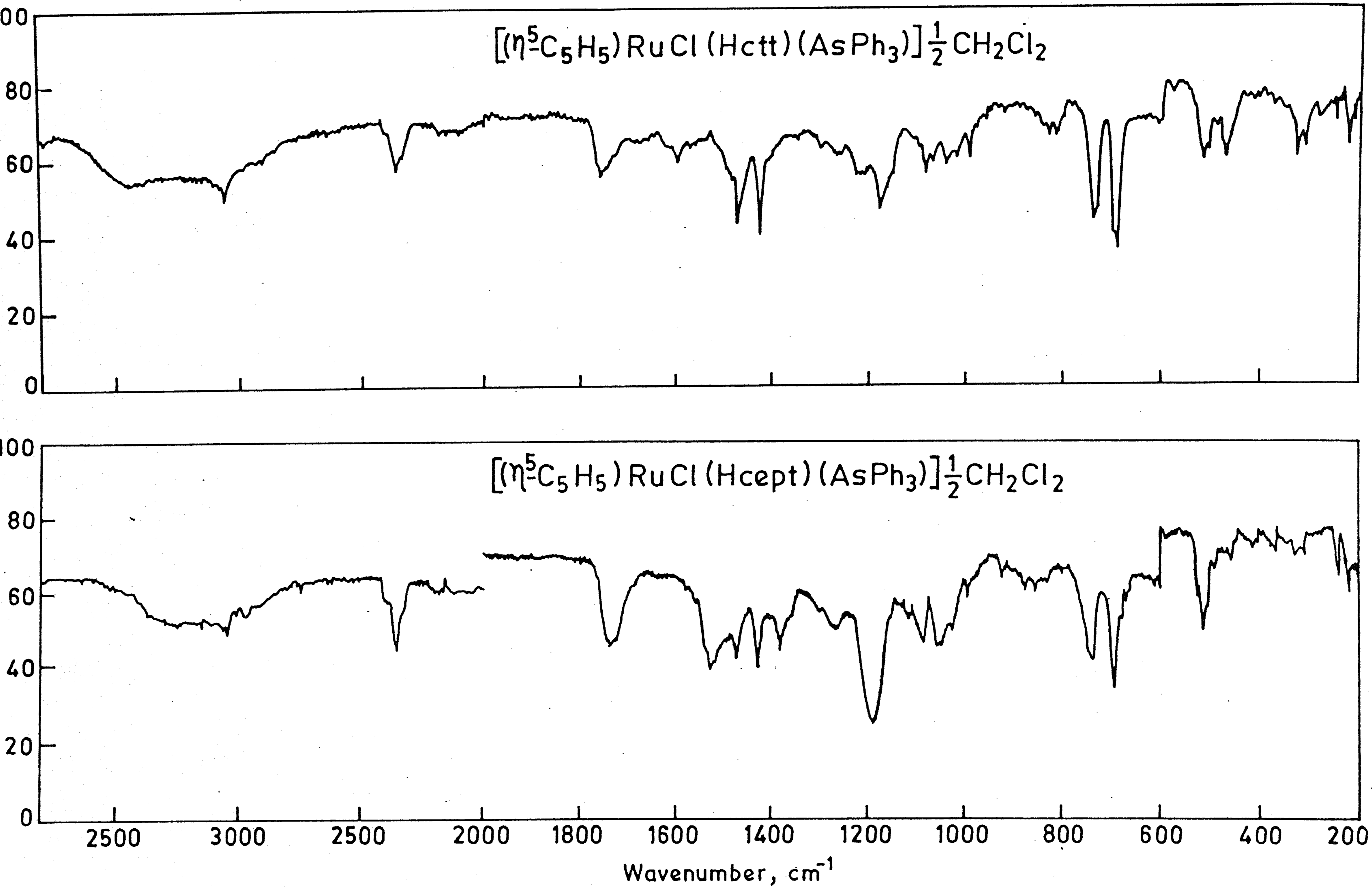
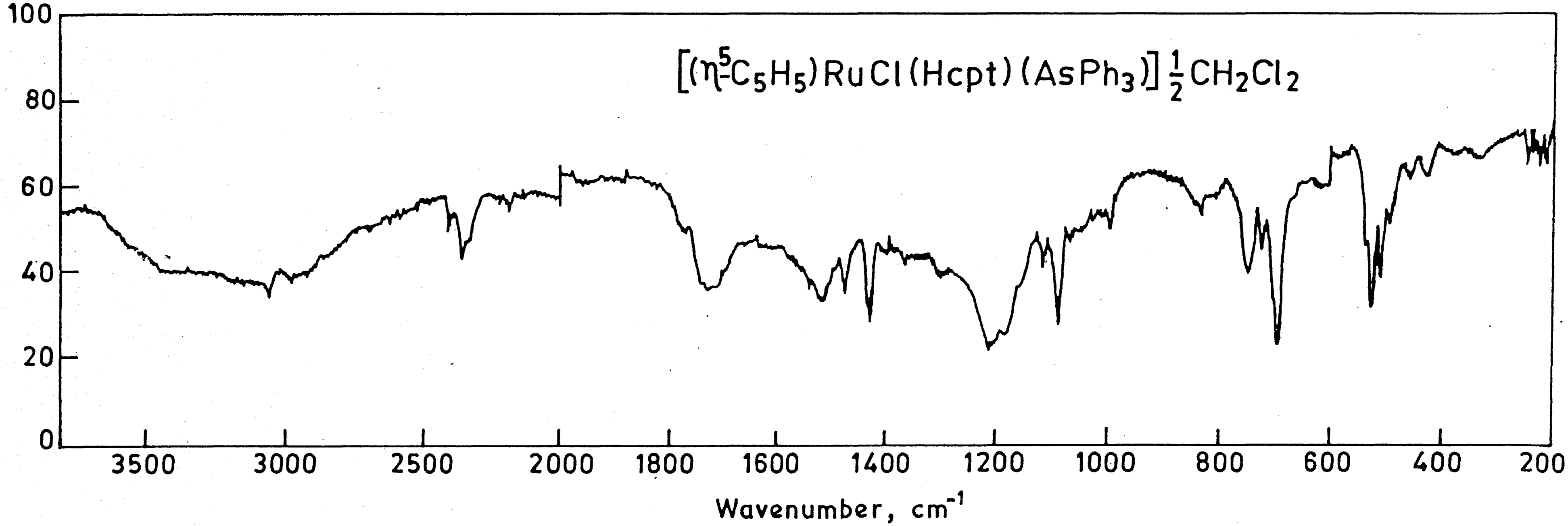
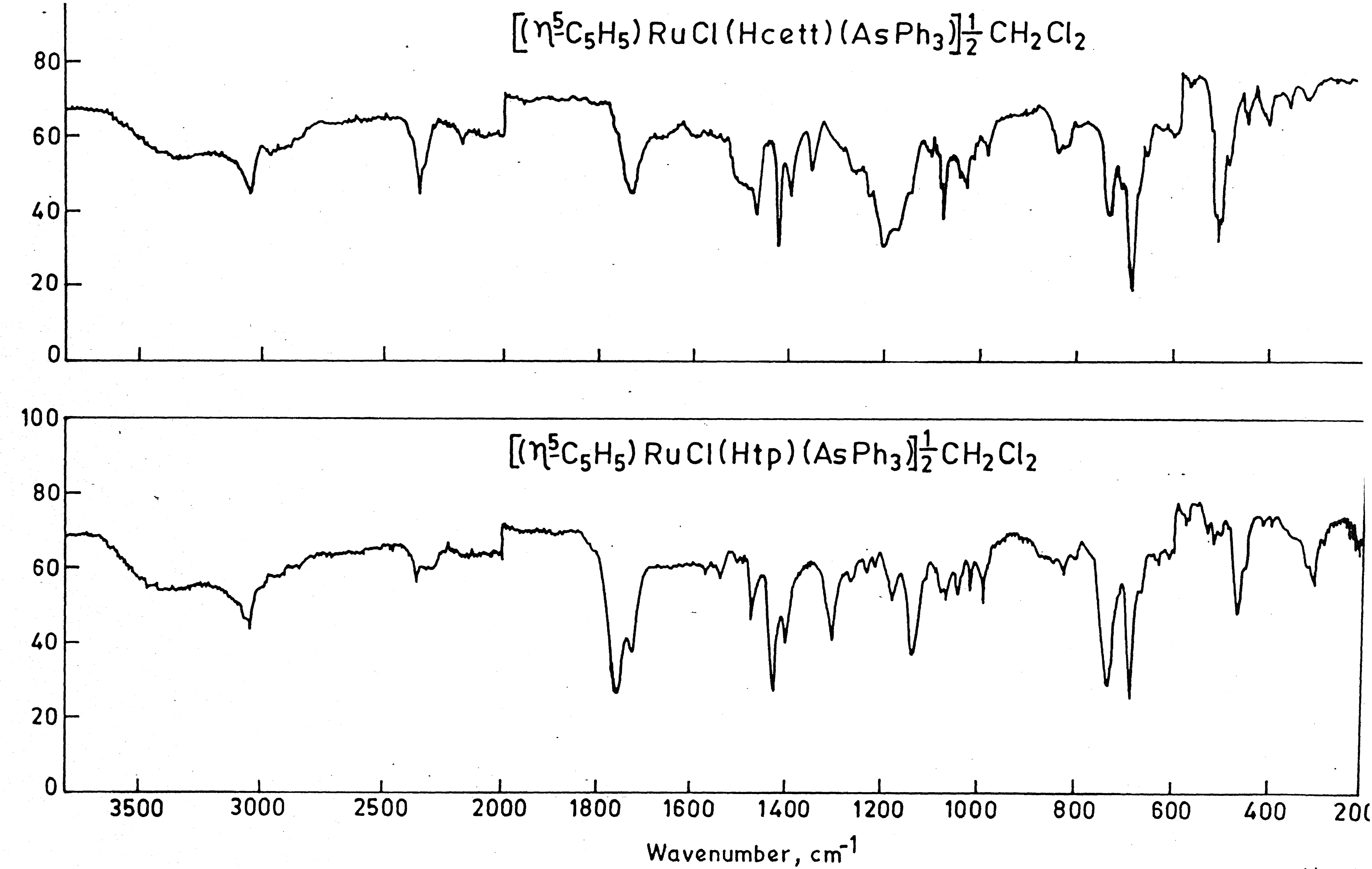

$[(\eta^5\text{-}C_5H_5)RuCl(Hctt)(AsPh_3)]\frac{1}{2}CH_2Cl_2$
$[(\eta^5\text{-}C_5H_5)RuCl(Hcept)(AsPh_3)]\frac{1}{2}CH_2Cl_2$
100
80
60
40
20
0
2500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig. V. 10



$[(\eta^5\text{-}C_5H_5)RuCl(Hcpt)(AsPh_3)]\frac{1}{2}CH_2Cl_2$
100
80
60
40
20
0
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig.V.11



[$(\eta^5$-$C_5H_5)RuCl(Hcett)(AsPh_3)]\frac{1}{2}CH_2Cl_2$
[$(\eta^5$-$C_5H_5)RuCl(Htp)(AsPh_3)]\frac{1}{2}CH_2Cl_2$
0
20
40
60
80
100
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
Wavenumber, cm^{-1}

Fig. V.12

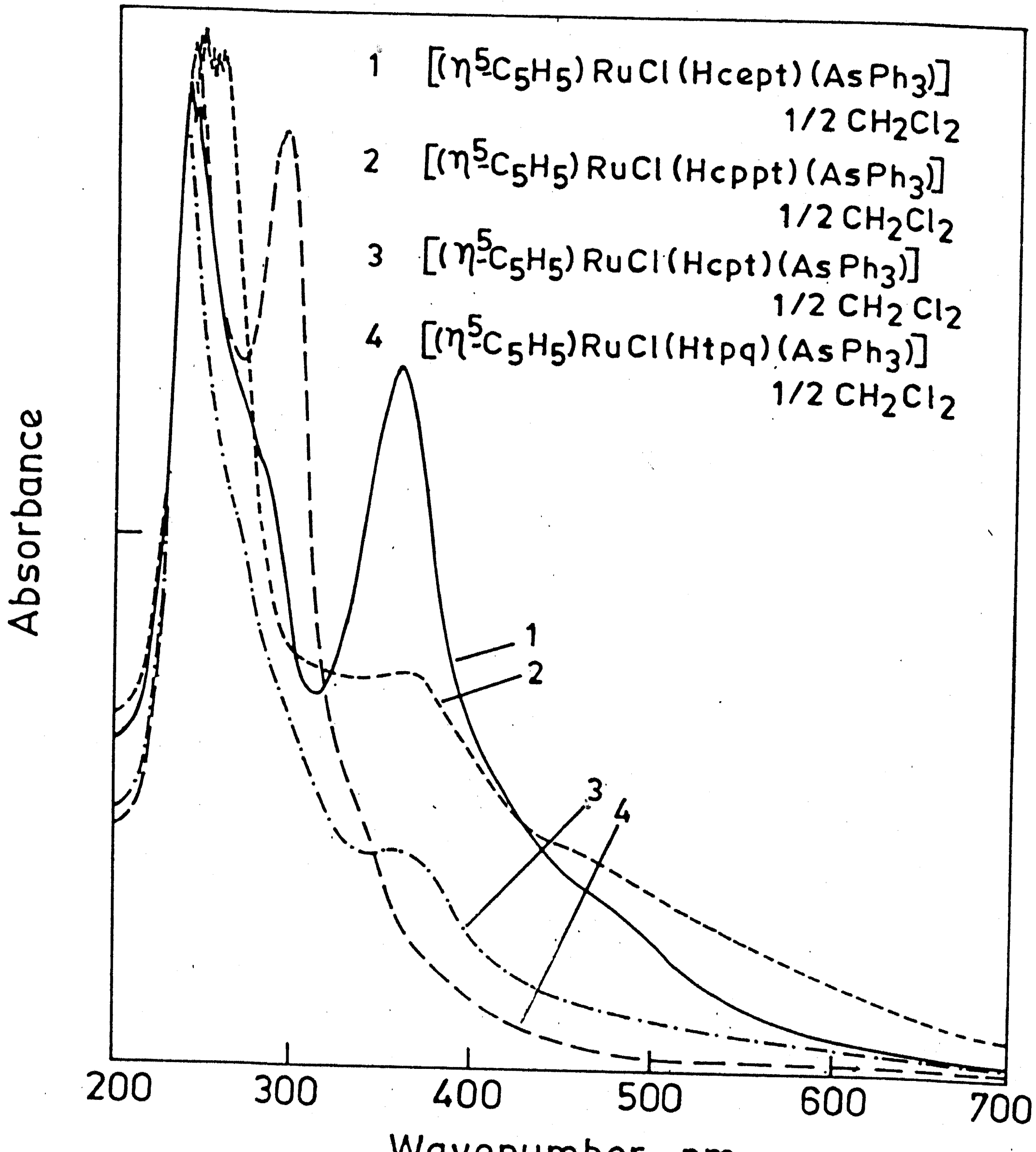
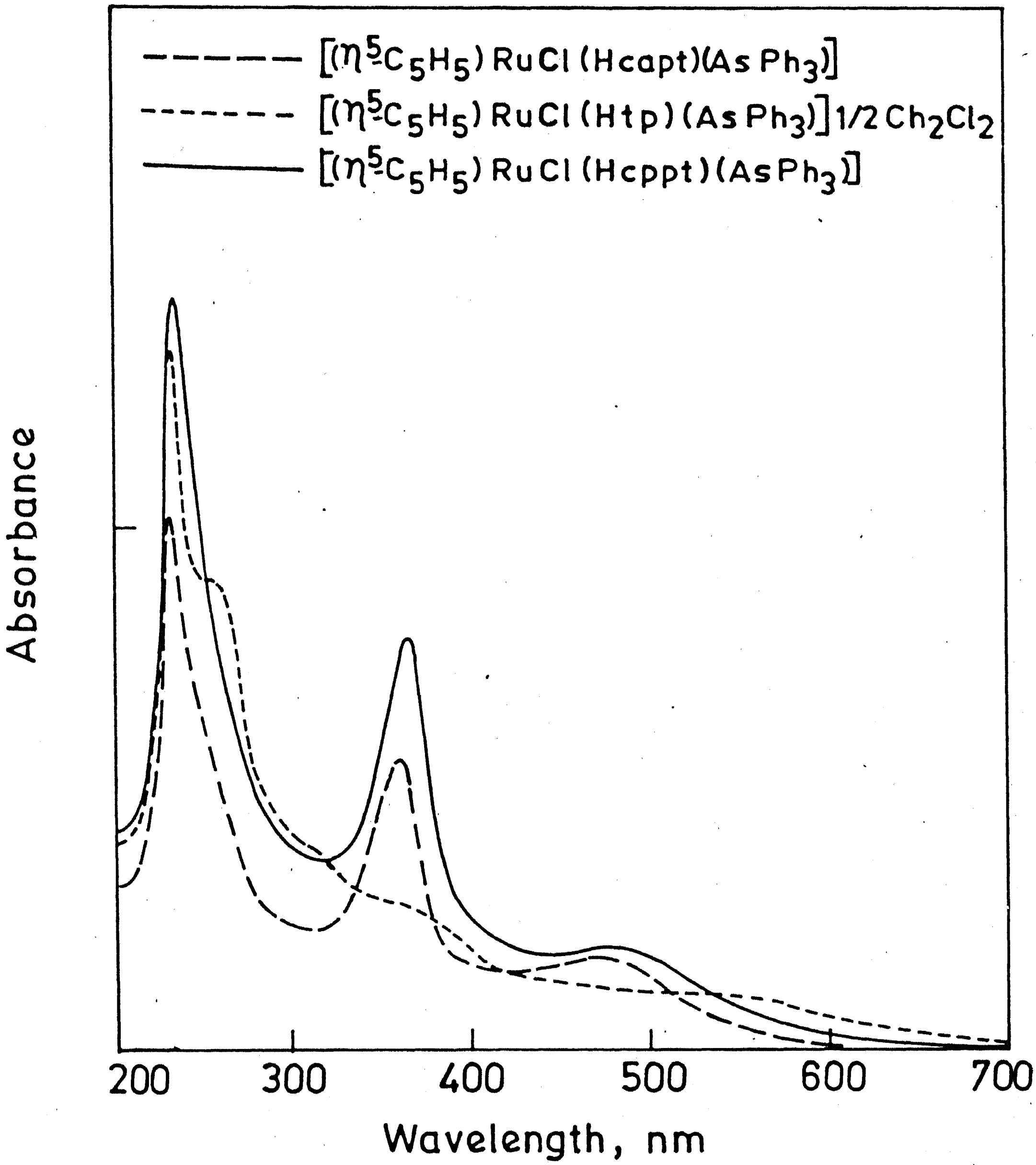

1 [(η5-C5H5) RuCl (Hcept) (AsPh3)] 1/2 CH2Cl2
2 [(η5-C5H5) RuCl (Hcppt) (AsPh3)] 1/2 CH2Cl2
3 [(η5-C5H5) RuCl (Hcpt) (AsPh3)] 1/2 CH2Cl2
4 [(η5-C5H5) RuCl (Htpq) (AsPh3)] 1/2 CH2Cl2
Absorbance
200
300
400
500
600
700
Wavenumber, nm
1
2
3
4

Fig. V.13



------ [$(\eta^5$-$C_5H_5)$ RuCl (Hcapt)($AsPh_3$)]
------- [$(\eta^5$-$C_5H_5)$ RuCl (Htp) ($AsPh_3$)] 1/2 CH_2Cl_2
——— [$(\eta^5$-$C_5H_5)$ RuCl (Hcppt) ($AsPh_3$)]
Absorbance
200
300
400
500
600
700
Wavelength, nm

Fig. V. 14

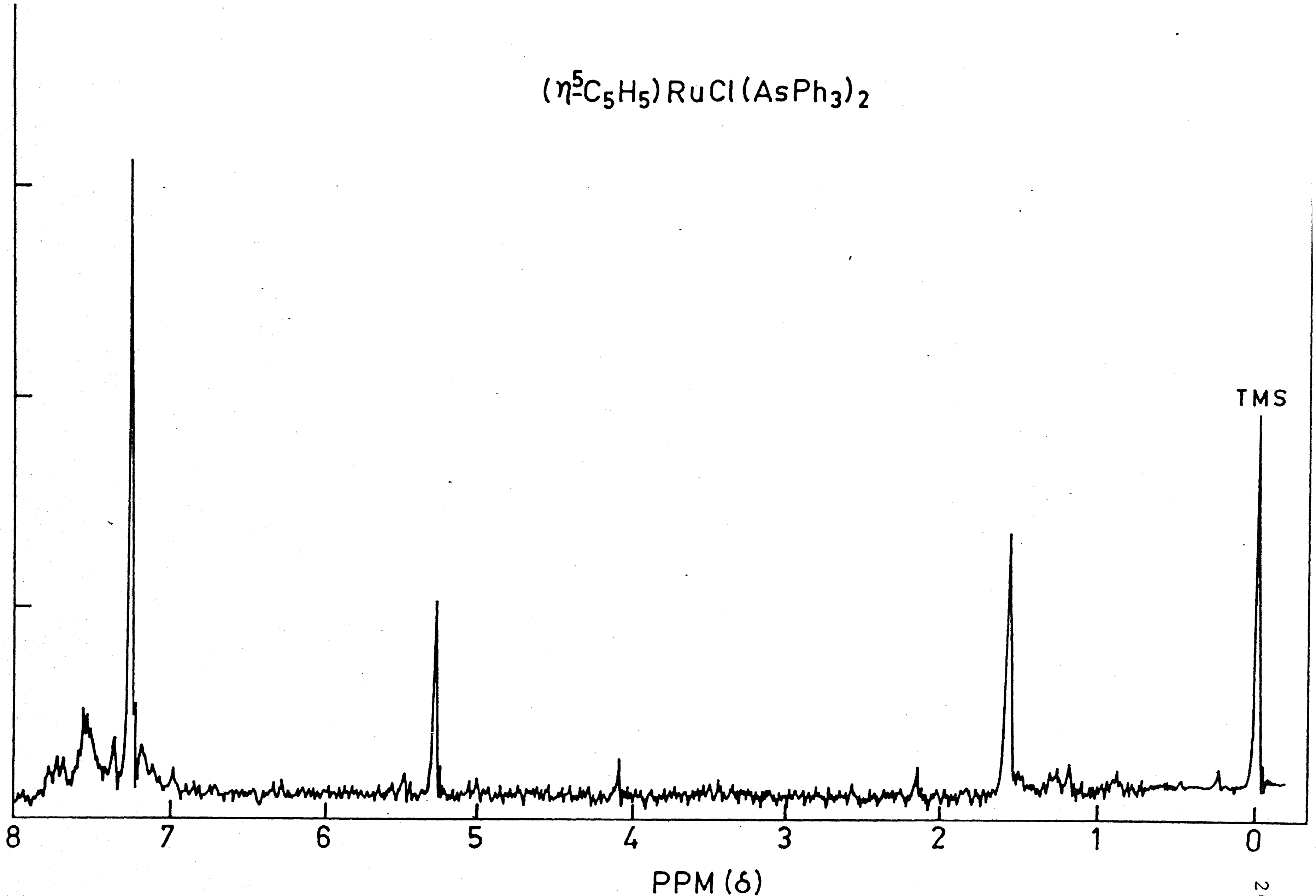


Fig. V.15

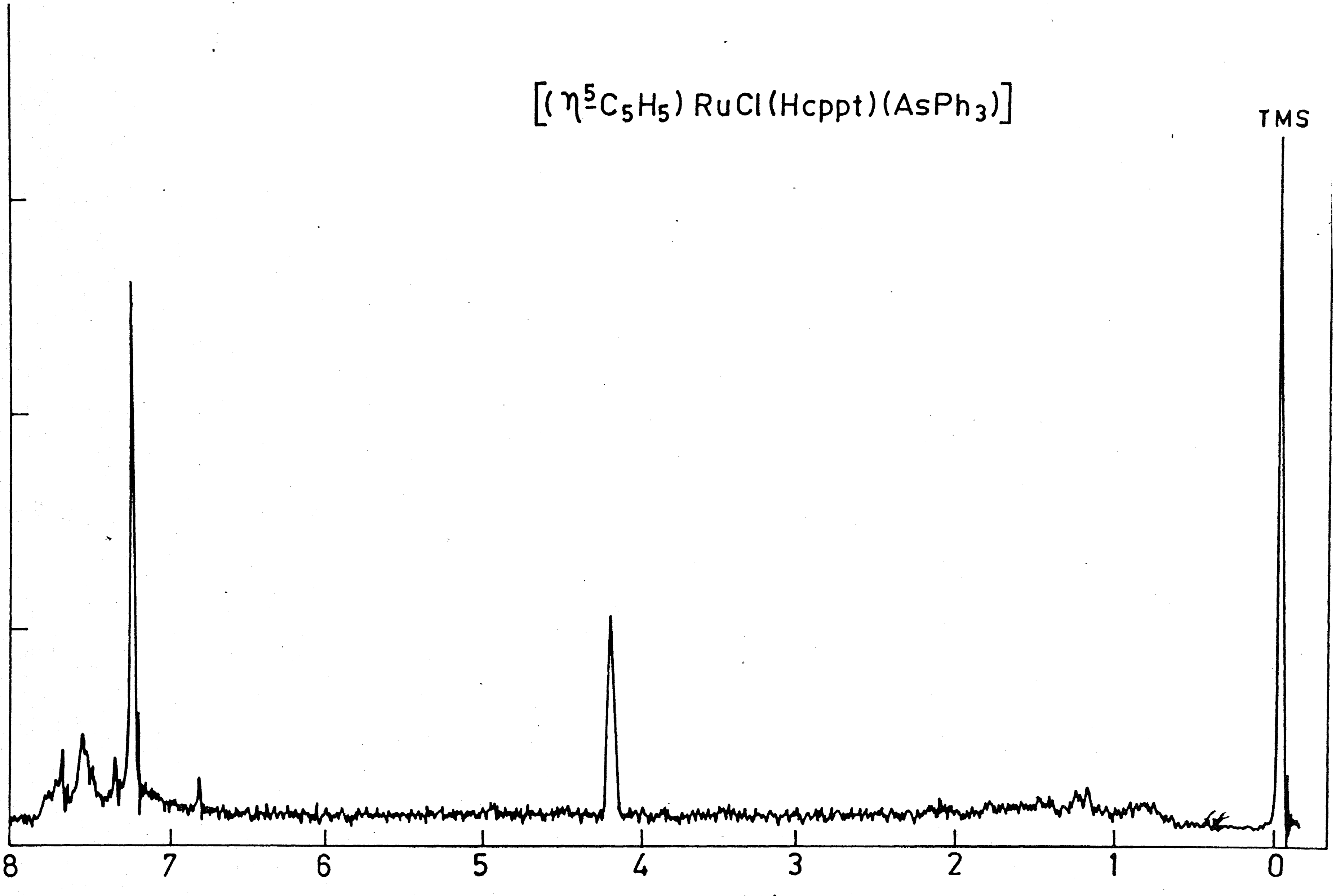


Fig. V.16

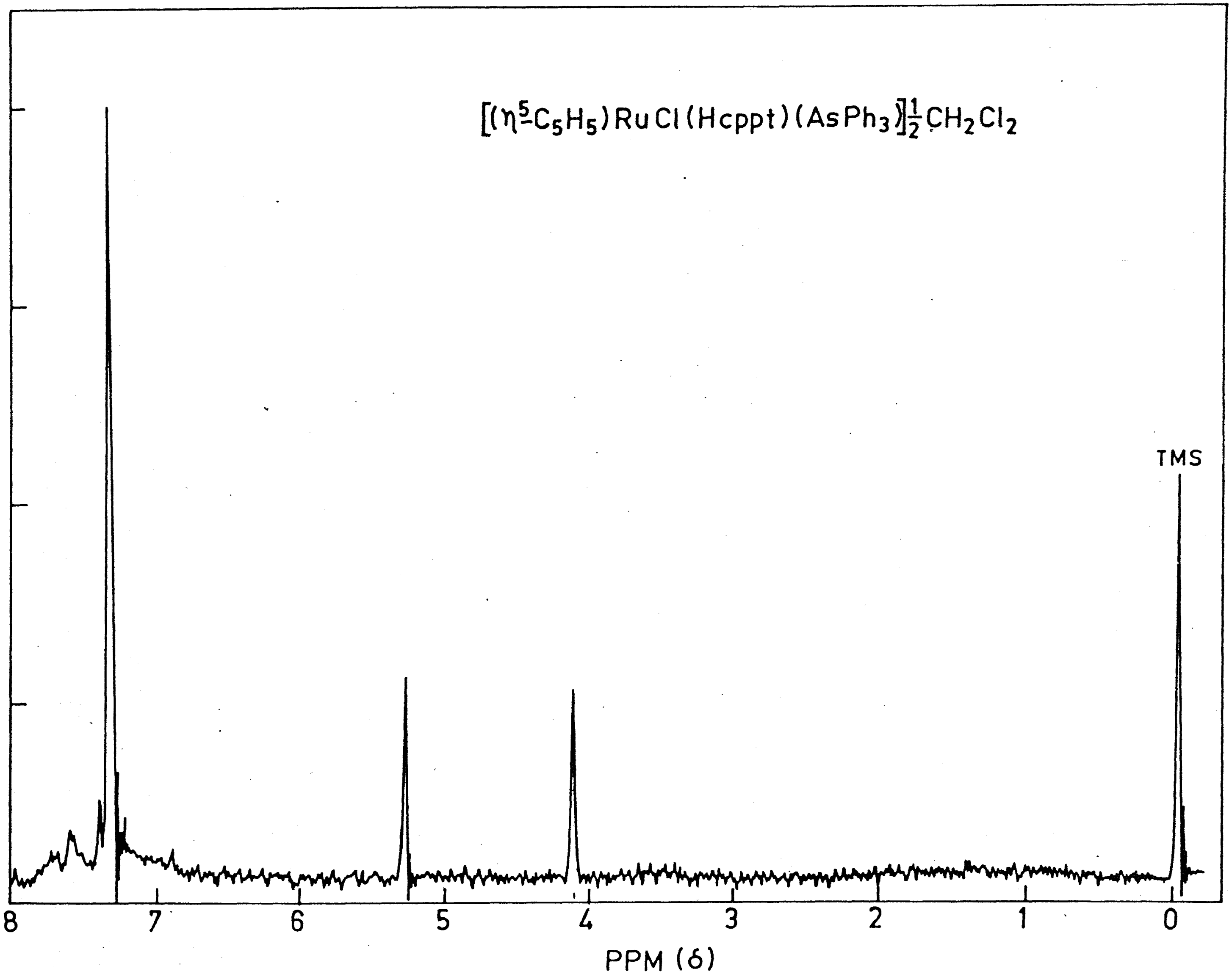


Fig.V.17

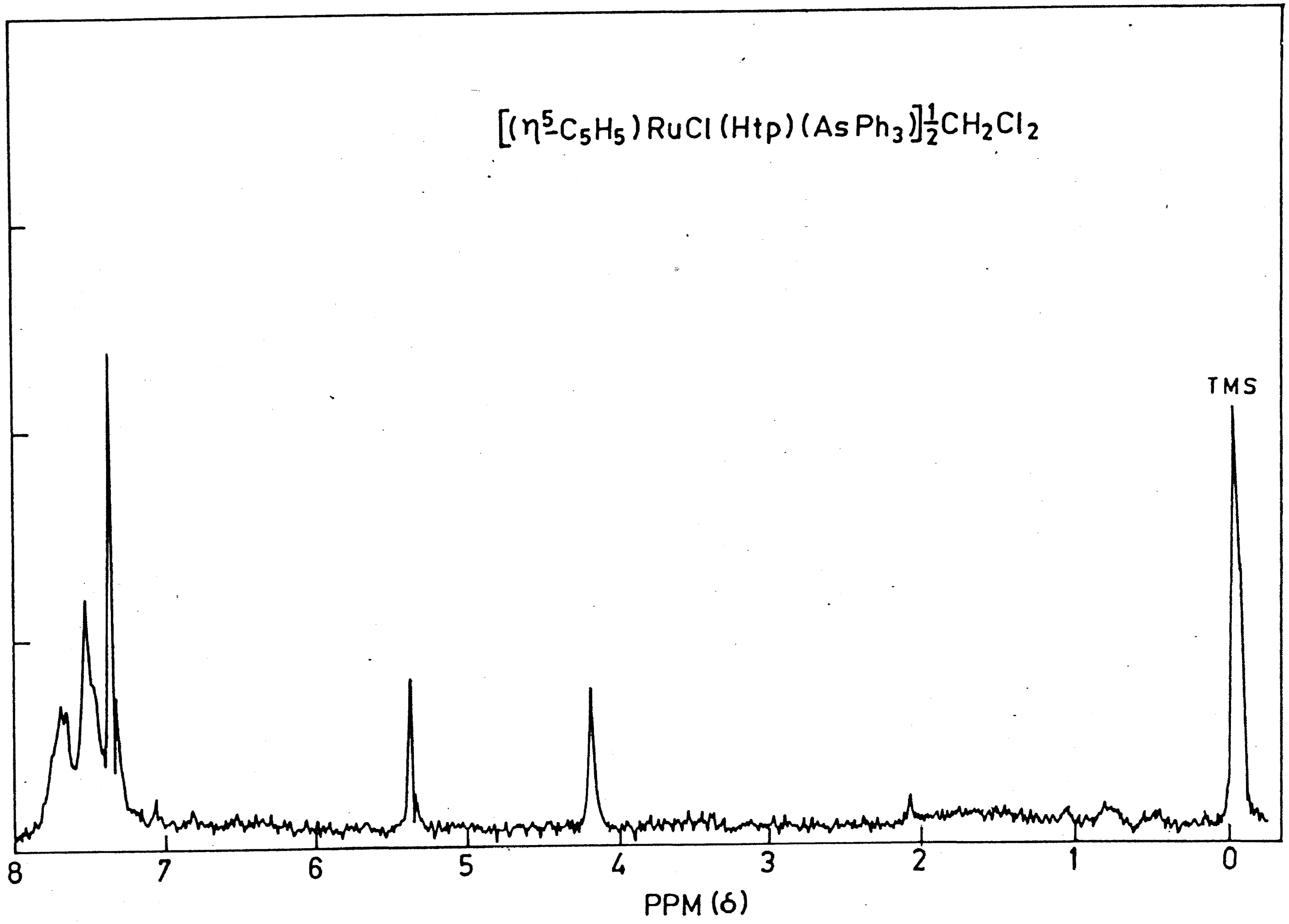


Fig.V.18

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APPENDIX

The ligands N-carboethoxy-4-toluene thioamide (Hctt), N-carboethoxy-2-pyrrole thioamide (Hcept), N-carboethoxy-1-pyrrole thioamide (Hcpt), N-carboethoxy-2-thiophene thioamide (Hcett), N-carboamido-2-pyrrole thioamide (Hcapt), N-carbophenylamido-2-pyrrole thioamide (Hcppt) and 2-thiopyrrole-1,2-dicarboximide (Htp) were prepared by literature methods.[1-3] The first step in the syntheses of these ligands is to prepare ethoxycarbonylisothiocyanate (SCNCOOEt).[4,5] A short description for the preparations of the ethoxycarbonylisothiocyanate and ligands are given below:

(1) Ethoxycarbonylisothiocyanate (SCNCOOEt)

A mixture of 700 ml of dry acetonitrile and 194 g (2.0 mol) of potassium thiocyanate was warmed on a steam bath. The warm mixture was treated, portionwise, with 217 g (2.0 mol) of ethylchloroformate. Heating was continued until the reaction mixture became hot and inorganic precipitate thickened rapidly. At this point the mixture became yellow. The heat source was removed and reaction was allowed to run its course. The mixture was permitted to cool slowly at room temperature, chilled, and suction filtered. The filtrate was concentrated under reduced pressure and the residual oil distilled; yield 161 g (b.p. 51-55°C/13 mm). Redistillation at 10 mm showed that the bulk of the material distilled at 44-46°C.

(2) N-Carboethoxy-4-toluene thioamide (Hctt)

To a stirred cold (ice bath) solution of 0.050 mol of toluene and 6.5 g (0.050 mol) of ethoxycarbonylisothiocyanate in 30 ml of CH_2Cl_2 was added 13.3 g (0.10 mol) of anhydrous $AlCl_3$ in small portions (15 20 min) at 0-3°C. The reaction mixture was stirred at this temp. for 4 hrs and then it was hydrolysed by careful addition of ice and dilute HCl. Enough CH_2Cl_2 was added to dissolve any solid organic material and the resulting solution was extracted with four 50 ml portions of 10% aqueous NaOH. This extract was washed with ethyl ether and acidified with conc. HCl (ice bath) to yield an oil which solidified upon cooling. The solid material was washed successively with dil. HCl and H_2O, dried and washed again with petroleum ether (30-60°C) or cold ethyl ether or cold aqueous ethanol. Purification of the crude product was accomplished by recrystallisation from petroleum ether (30- 0°C), m.p. 98-100°C.

(3) N-Carboethoxy-2-pyrrole-thioamide (Hcept)

A mixture of 16.8 g (2.25 mol) of pyrrole and 32.8 g (0.25 mol) of ethoxycarbonylisothiocyanate, both ice cold, was swirled occasionally and cooled as needed to prevent its temperature from rising above 40°C. Within an hour the mixture had solidified, whereupon it was allowed to stand overnight. Following repeated washing of the product with petroleum ether (b.p. 60-90°C), 46.2 g (93%) of Hcept was obtained. Recrystallization from aqueous

ethanol gave the pure compound, m.p. 98.5-99.5°C.

(4) N-Carboethoxy-1-pyrrole-thioamide (Hcpt)

Pyrrole-potassium was prepared in a nitrogen atmosphere by the gentle refluxing of a stirred mixture of 40.2 g (0.60 mol) of pyrrole, 100 ml of THF and 19.5 g (0.50 g-atom) of potassium, until all the metal had reacted. Following dilution with 150 ml of solvent and chilling of the slurry in an ice-salt bath, there was introduced a solution of 59.0 g (0.45 mol) of ethoxycarbonylisothiocyanate in 100 ml of THF, dropwise, at such a rate that the reaction temperature was kept below 10°C (addition time: 1.5 hr). The reaction mixture was stirred for a further 0.5 hr, then it was mixed with 450 ml of absolute ether and filtered. The potassium salt thus obtained was dissolved in water, and the resulting solution was washed with ether chilled and acidified with acetic acid, which yielded crude product (45% yield), m.p. 77-80°C and recrystallization from petroleum ether (60-80°C) afforded the pure compound as yellow needles, mp. 80-81°C.

(5) N-Carboethoxy-2-thiophene-thioamide (Hcett)

A mixture of 8.4 g (0.10 mol) of thiophene 13.1 g (0.10 mol) of ethoxycarbonylisothiocyanate and 10 ml of anhydrous stannic chloride solidified completely when allow to stand for 4 hr and the resulting solid was ground into a powder and thoroughly mixed with dilute hydrochloric acid. Filtration followed by washing of the precipitate first with dilute hydrochloric acid and then

with water yielded 17.5 g (81%) of crude N-carboethoxy-2-thiophenethioamide (Hcett), m.p. 101-103°C. Recrystallization from carbon tetrachloride yielded the pure compound as dark red crystals, m.p. 107-108°C.

(6) N-Carboamido-2-pyrrole- hioamide (Hcapt)

A solution of Htp (1 g) in 2 ml of concentrated aqueous ammonia was allowed for four to five minutes whereupon a precipitate of Hcapt was formed which was collected by filtration. The yield of the crude product was 0.80 g (73%) (m.p. 169-170°C). The product was further purified in the form of yellow crystals by crystallization from hot water, m.p. 171-172°C.

(7) N-Carbophenylamido-2-pyrrole-thioamide (Hcppt)

A mixture of 1.0 g of Hcept and 5 ml of anili was boiled for about one minute and the resulting solution was cooled and then filtered. Following washing of the precipitate with carbon tetrachloride, there was obtained 1.1 g (92%) of N-carbophenylamido-2-pyrrolethioamide. Recrystallization from ethanol yielded the pure compound in the form of yellow crystals, m.p. 213-214°C.

(8) 2-Thiopyrrole-1,2-dicarboximide (Htp)

A mixture of 5.0 g of Hcept and 15 ml of quinoline was heated in a 25 ml erlenmeyer flask until the temperature of the

escaping vapours reached 170-180°C. The resulting tarry material was cooled, subsequently mixed with cold, dilute hydrochloric acid and extracted with ether. The ether extract was washed with water treated with charcoal and dried with $MgSO_4$, finally it was evaporated to dryness to yield 3.3 g (87%) of Htp, m.p. 135-138°C. Recrystallization from aqueous ethanol gave the product in the form of orange crystals, m.p. 140-141°C.

(9) 2-Thione-3-phenyl-4-quinazolinone[6]

A mixture of equimolar quantities of phenylisothiocyanate, C_6H_5NCS (6 ml) and anthranilic acid (6 g) in absolute alcohol (70 ml) was refluxed for 6 hr. The product was washed with ethanol, containing sodium hydroxide (10%, w/v), reprecipitated by HCl, filtered and washed several times with water and dried at 60-70°C. The compound was recrystallized from hot ethanol. The colourless compound melts at 190°C.

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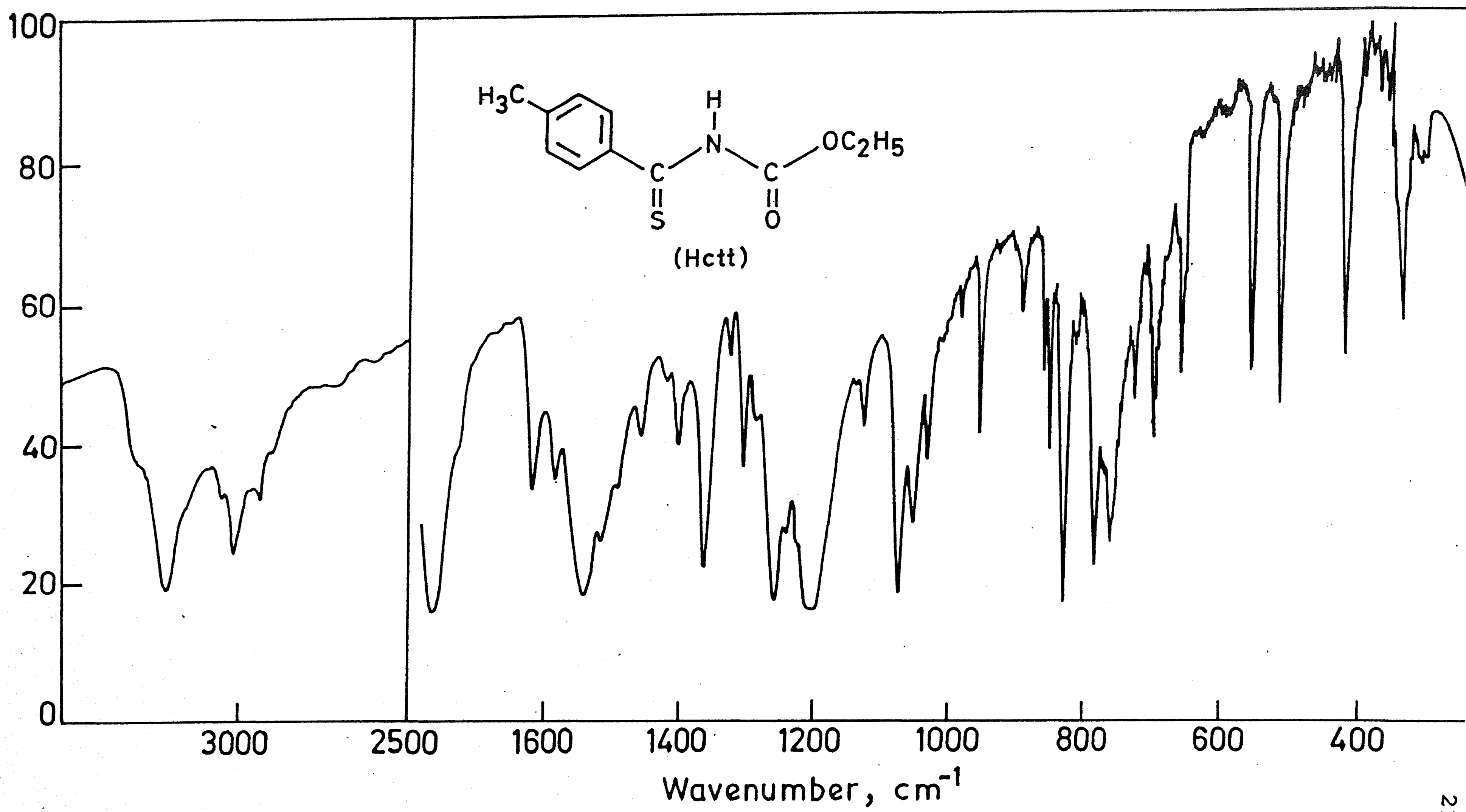
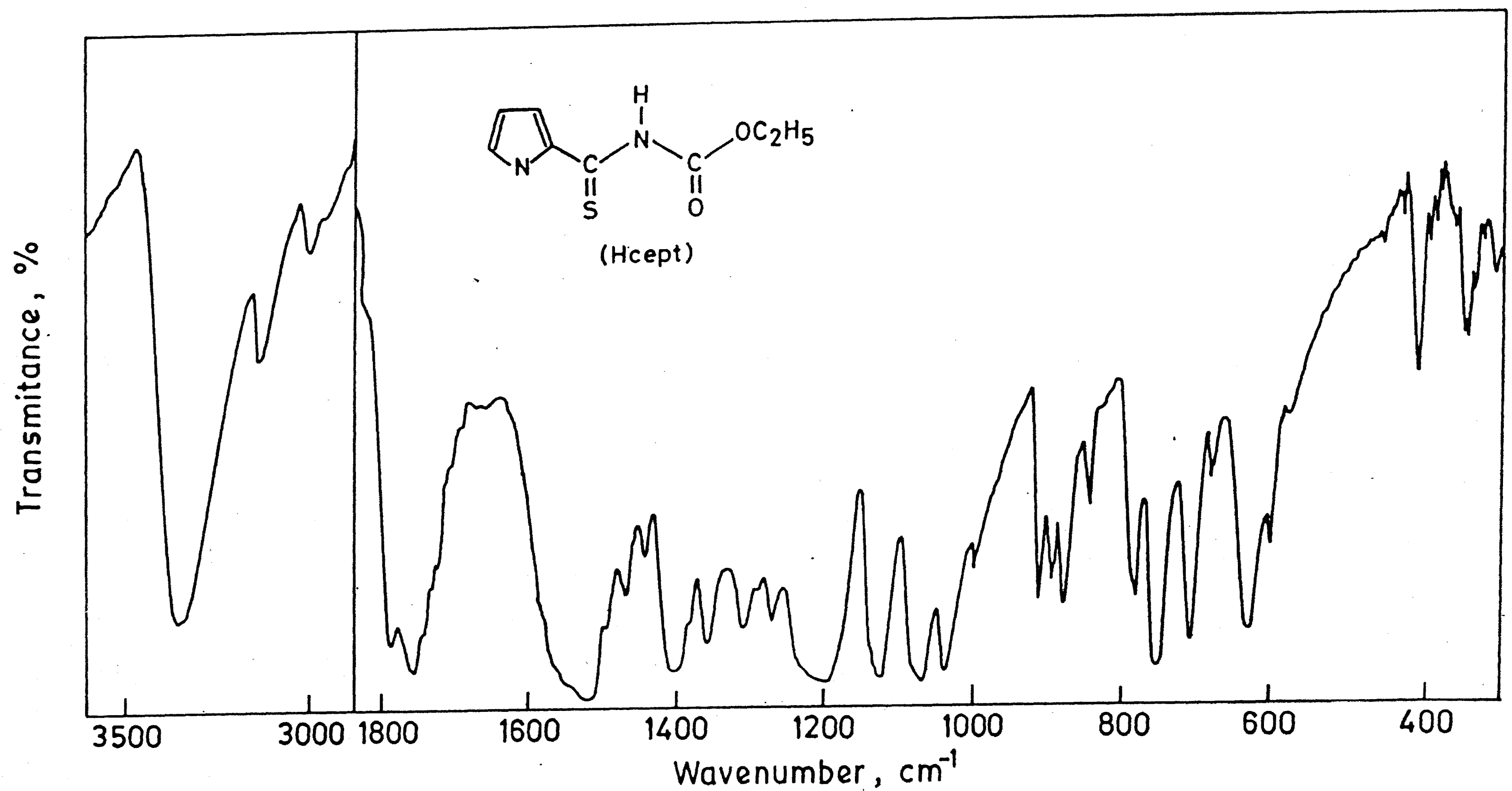

H3C
H
N
C
S
C
O
OC2H5
(Hctt)
100
80
60
40
20
0
3000
2500
1600
1400
1200
1000
800
600
400
Wavenumber, cm-1

Fig. A.1



(Hcept)
Transmitance, %
3500
3000
1800
1600
1400
1200
1000
800
600
400
Wavenumber, cm^{-1}

Fig. A.2

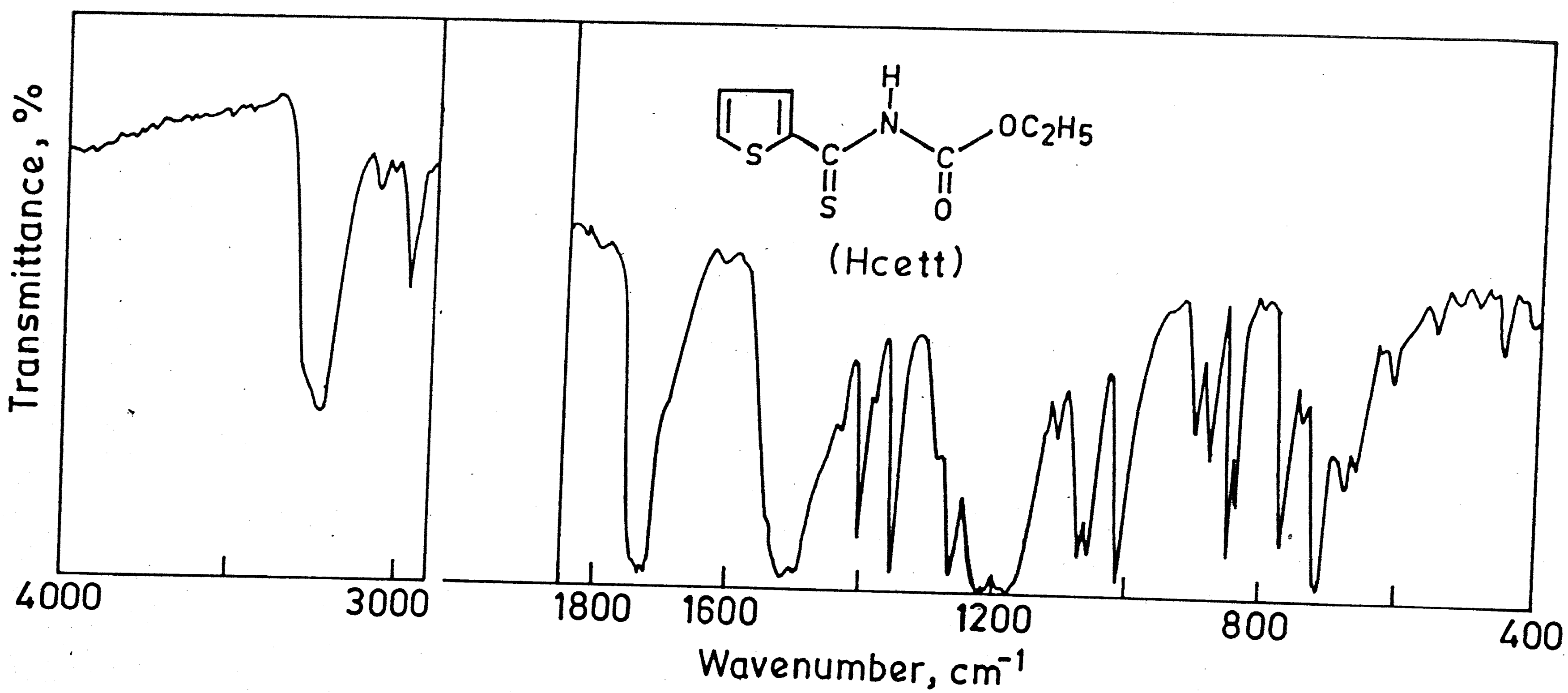

Transmittance, %
(Hcett)
4000
3000
1800
1600
1200
800
400
Wavenumber, cm^{-1}

Fig. A.3

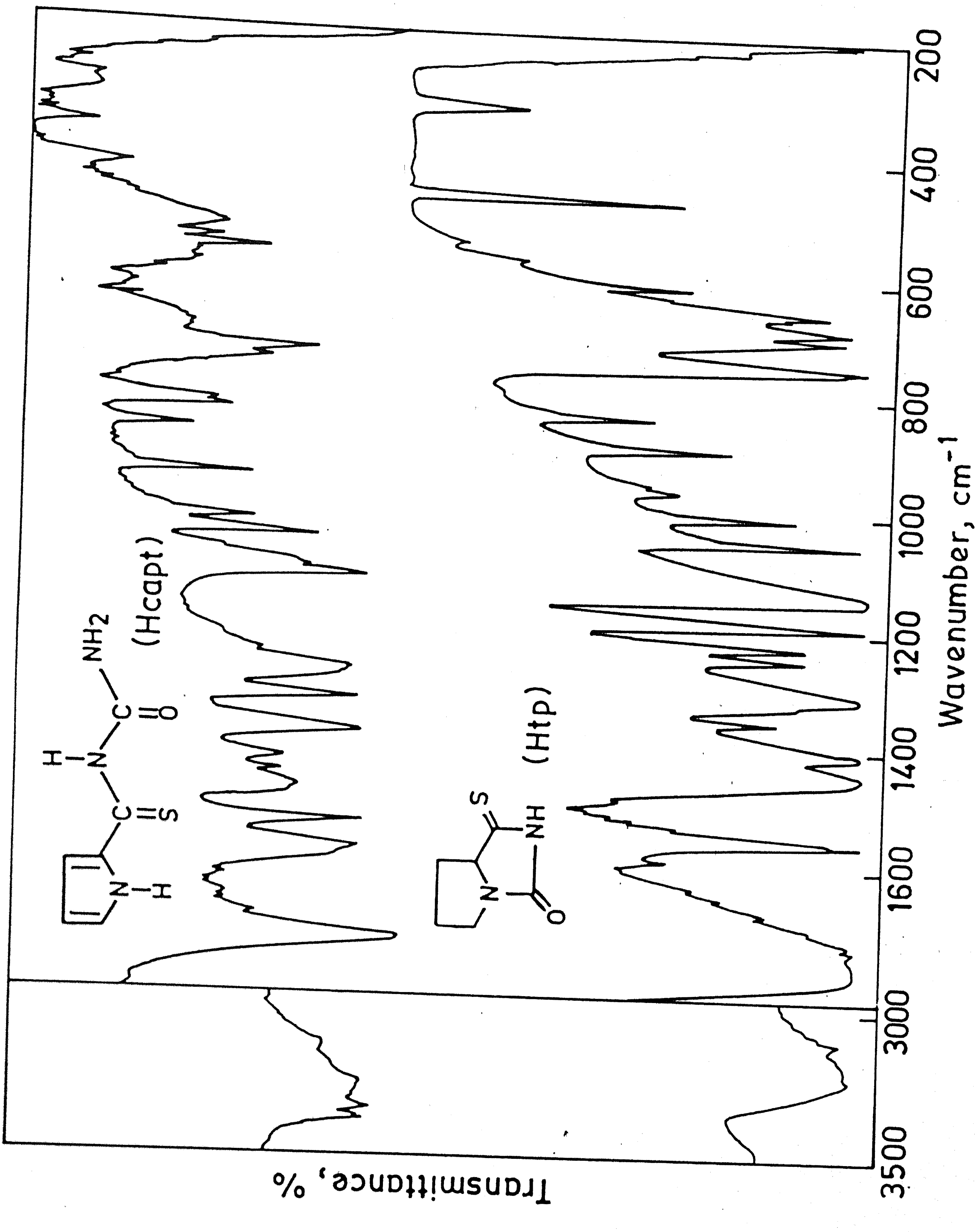

(Hcapt)
(Htp)
Transmittance, %
Wavenumber, cm^{-1}
3500
3000
1600
1400
1200
1000
800
600
400
200

Fig. A.4

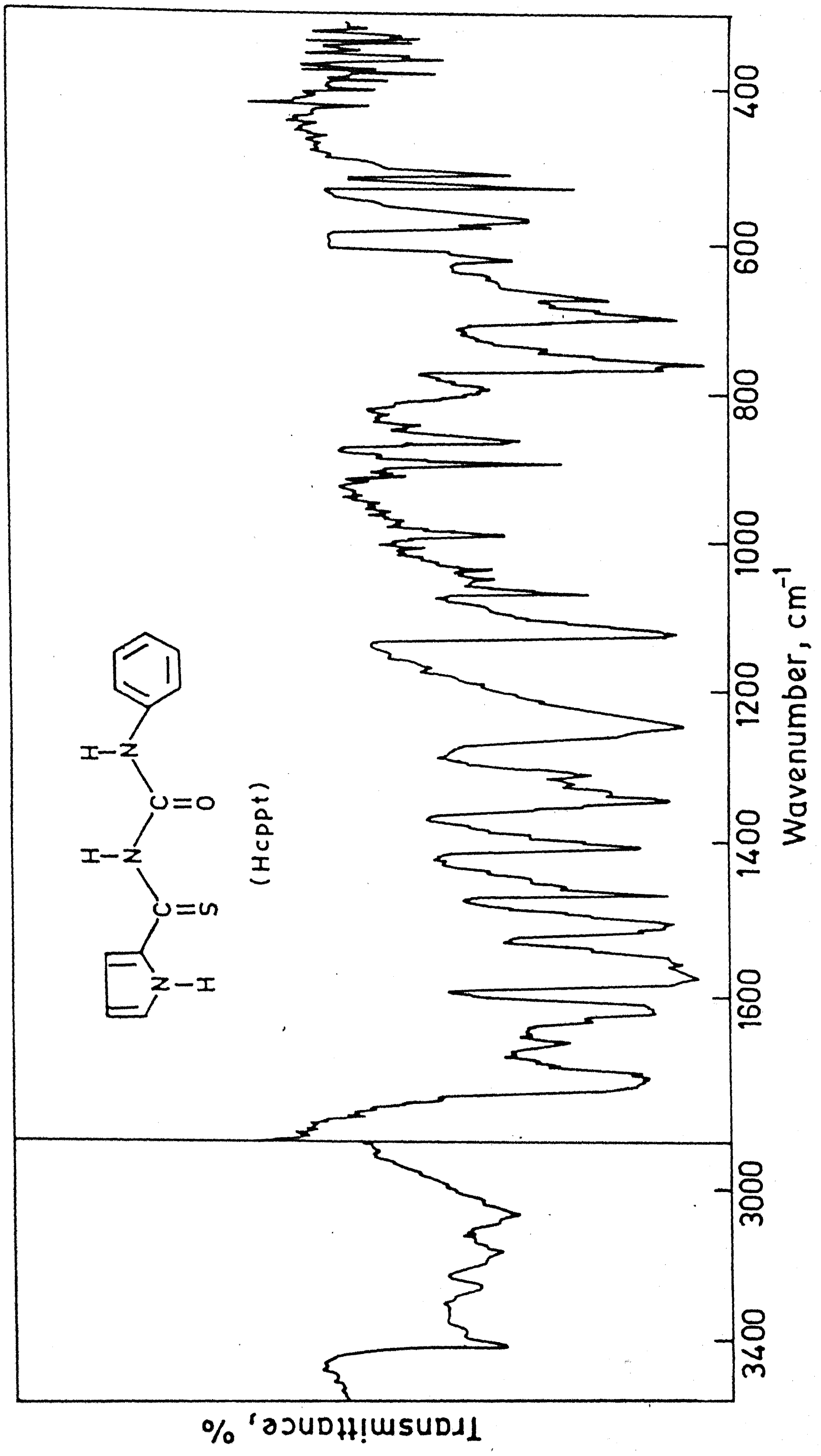
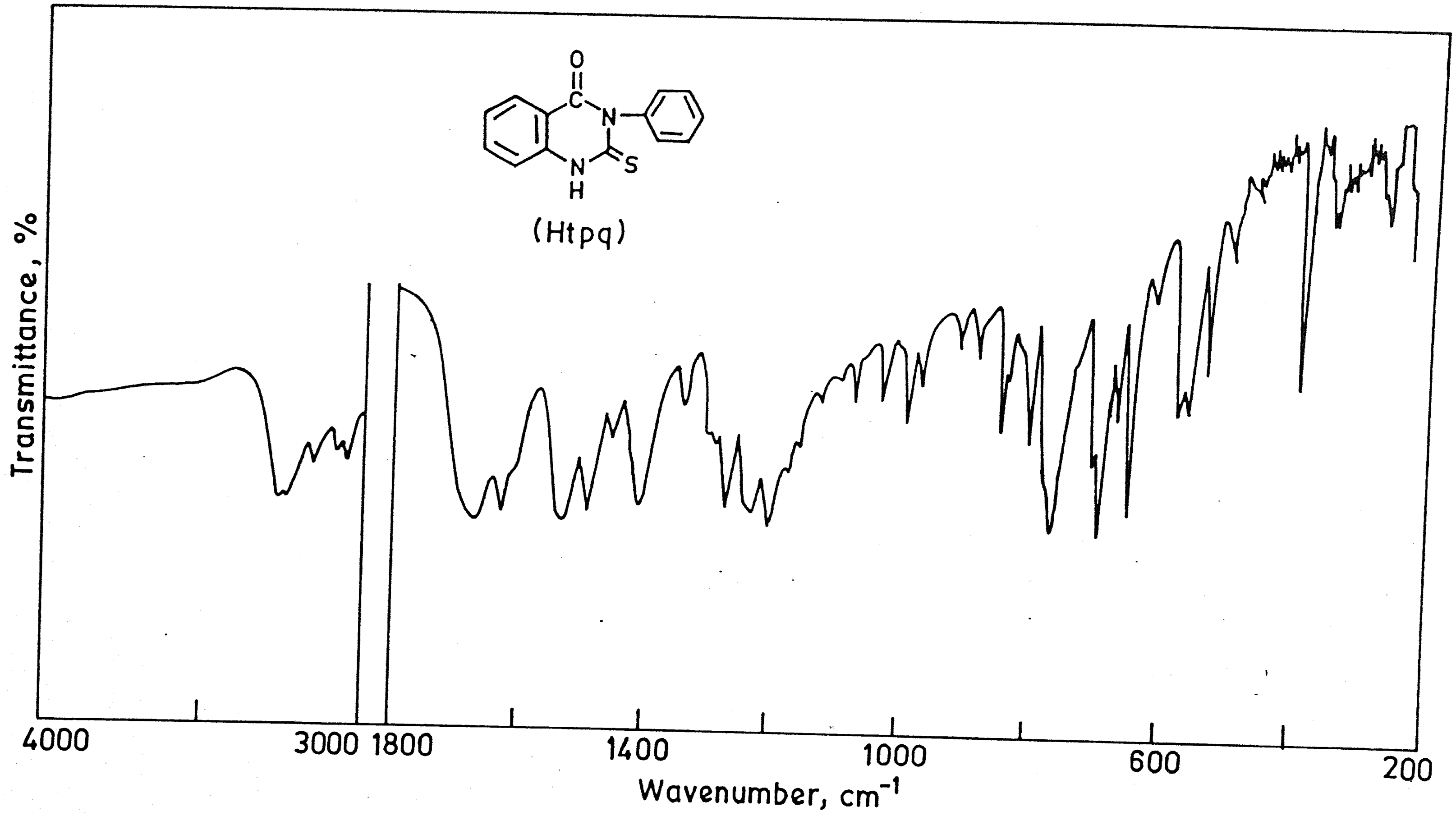

(Hcppt)
Transmittance, %
Wavenumber, cm^{-1}
3400
3000
1600
1400
1200
1000
800
600
400

Fig. A.5



O
C
N
N
H
S
(Htpq)
Transmittance, %
4000
3000
1800
1400
1000
600
200
Wavenumber, cm^{-1}

Fig. A.6

LIST OF PUBLICATIONS

1. Reactions of N-ethoxycarbonyltoluene-4-thiocarboxamide (ETTH), N-ethoxycarbonylpyrrole-2-thiocarboxamide (ETH), 2-thiopyrrole-1,2-dicarboximide (TPH) and N-carbamoylpyrrole-2-thiocarboxamide (CPTH) with $[Cu^{I}(MPh_3)_3X]$ (M = P or As; X = Cl, Br or I] and Ag(I), Cd(II), Hg(II) or Pb(II) ions,
   Veena Chauhan and Sheo K. Dikshit,
   Transition Met. Chem., 11, 223 (1986).

2. Thiocarboxamide complexes of Rhodium, Copper, Palladium and Platinum. The synthesis of $[CuX(C_4H_4NCSNHCO_2Et)(MPh_3)_2]$ (X = Cl or Br; M = As or P), $[RhCl(MeC_6H_4CSNHCO_2Et)_2(PPh_3)]$ and $[M(MeC_6H_4CSNHCOOEt)_2(PPh_3)_2]$ (M = Pd or Pt),
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   Inorg. Chim. Acta, 000 (1987), under print.

6. Mixed ruthenium carbonyls: Reaction of cis-$[Ru(CO)_2Cl_2]$ with some thiocarboxa(i)mides,
   Veena Chauhan and S.K. Dikshit,
   communicated.

List of publications (contd.)

7. Cyclopentadienyl ruthenium(II) complexes: Reactions of $[(\eta^5-C_5H_5)RuCl(AsPh_3)_2]$ with some thiocarboxa(i)mides,
Veena Chauhan and S.K. Dikshit,
(communicated).

8. Reactions of $Ru^{II}Cl_2(PPh_3)_3$ with aromatic thioamide ligands (ArCSNHCOR). Syntheses & characterization of Ru(II) complexes,
Veena Chauhan and S.K. Dikshit
(to be communicated).